Electronic Supporting Information for

Shining light on the excited state energy cascade in kinetically inert Ln(III) complexes of a coumarin-appended DO3A ligand

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Materials and methods

All solvents for spectroscopic experiments were of HPLC grade and used as received. Water was deionized and microfiltered using a Milli-Q Millipore machine. The complexes presented in this report were prepared *in situ*, characterization of the isolated ligand and complexes can be found in ref. 32. HEPES buffer and the lanthanide salts were purchased from Sigma Aldrich and used as received.

Sample preparation

The complexes ($1.14 * 10^{-5}$ M) were assembled *in situ* from stock solutions by mixing 1:1 equivalent of ligand (**L**) and lanthanide ions in aqueous 0.1 M HEPES buffer pH 7.4. The complexes were formed using the $Ln.Cl_3*6{\cdot}H_2O$ salts, Ln = Eu^{3+}, Gd^{3+}, Tb^{3+} or Y^{3+}. Oxygen was removed from the samples using a standard freeze-pump-thaw degassing method. The freeze−pump−thaw cycle was repeated five times to eliminate the oxygen in the samples and never backfilled with an inert gas (referred to as degassed condition).

Optical spectroscopy

Absorption spectra were measured with a Cary 300 UV-Vis double beam spectrometer from Agilent Technologies against air using a pure solvent as the baseline. The excitation and fluorescence spectra together with the fluorescence and metal centred lifetimes were measured with a FluoTime 300 instrument from PicoQuant. The excitation source was the 355 nm line from a VisUV laser or a Xenon Cw lamp from PicoQuant. The data were fitted as monoexponential or triexponential decay using the deconvolution as implemented in the FluoFit software (version 4.6.6) from PicoQuant. The phosphorescence measurements were done on a Cary Eclipse fluorescence spectrometer with a photomultiplier tube from Agilent Technologies. The phosphorescence decays were analysed and fitted to exponential decay functions using the Origin software package. All emission and excitation spectra and time-resolved emission decay profiles can be found in the following

For all spectroscopic measurements, the absorbance at the excitation wavelength was kept below 0.1 to avoid inner filter effects and intermolecular interactions. Absorption, excitation and fluorescence experiments at ambient temperatures were performed in a sealed 10.00 mm vacuum cuvette or 10.00 mm Hellma quartz fluorescent cuvettes. The phosphorescence experiments at 77 K were performed in a Dewar fitted with a quartz cold finger accessory; the sample solutions were placed in a NMR tube, positioned in the Dewar and flash frozen using liquid nitrogen.

Relative quantum yields.

Relative quantum yields were determined by single point determination using different laser intensity and calculated using eqn (1). Where ϕ is the fluorescence quantum yield, a is the slope from the plot of the integrated fluorescence intensity divided by the absorbance of the reference (Dr/Ar) vs. the integrated fluorescence intensity divided by the absorbance of the sample x (Dx/Ax), and n the refractive index of the

solvent. The subscripts ref and x denote reference and the sample respectively. The method is internally consistent but in our hands cannot be used to determine absolute quantum yields.

$$\phi_x = a \cdot \phi_{ref} \cdot \frac{{n_x}^2}{{n_r}^2} \tag{1}$$

For quantum yield calculations, an excitation wavelength of 355 nm was used for both the reference and sample. Quinine sulphate in 0.5 M sulfuric acid was used as the reference ($\phi_{ref} = 0.546$), all data can be found in the ESI. $n_{ref} = 1.346$ and $n_x = 1.339$.

Optical Spectroscopy: H_3.L

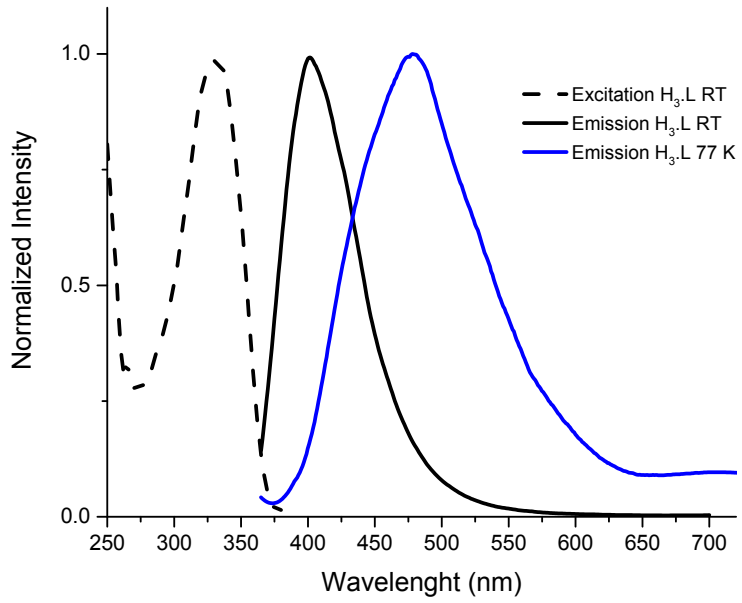


Figure S1. Excitation (followed at 402 nm) and emission (excitation 355 nm) spectra of a 1.14 $\cdot 10^{-5}$ M solution of **H_3.L** in HEPES buffer at pH 7.4 at room temperature. Phosphorescence spectrum of the same solution at 77 K, Gate time 1 ms, Delay 5 ms.

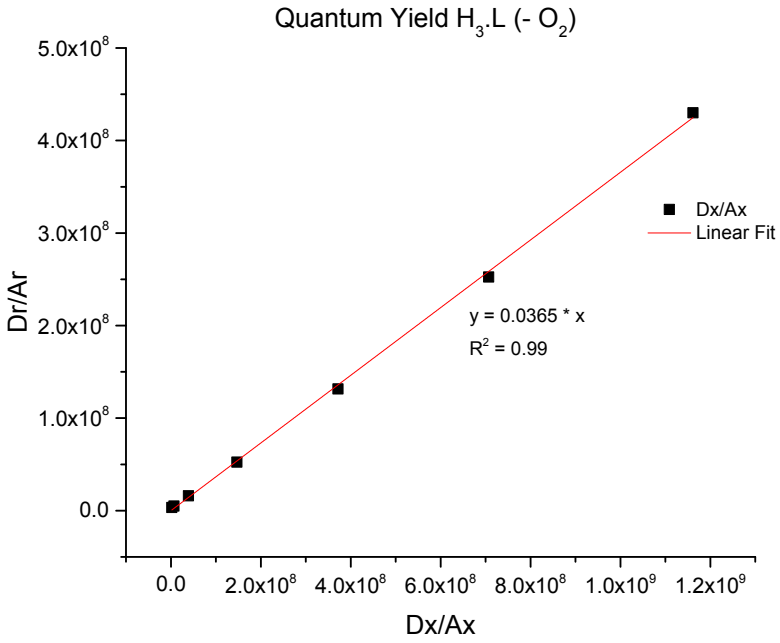


Figure S2. Quantum yield determination for **H_3.L** (- O_2) in 0.1 M HEPES buffer at pH 7.4 at room temperature.

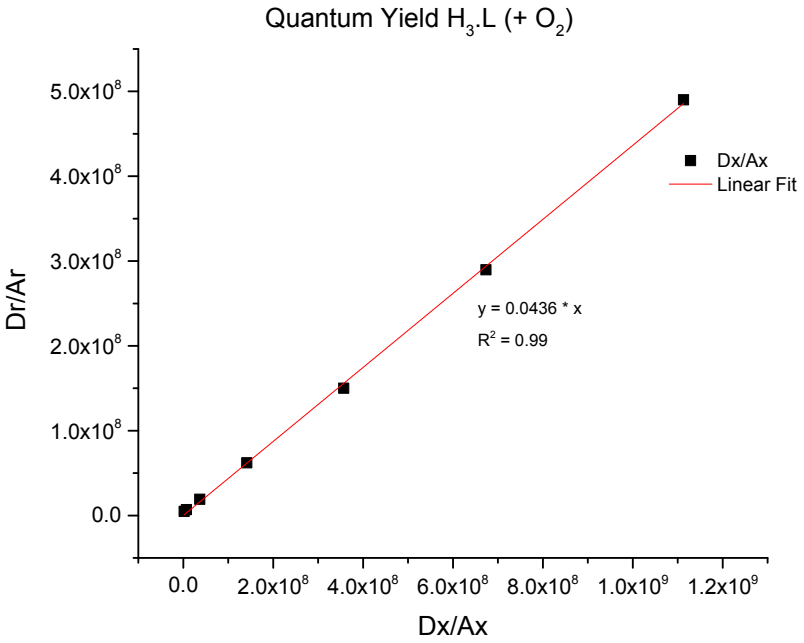
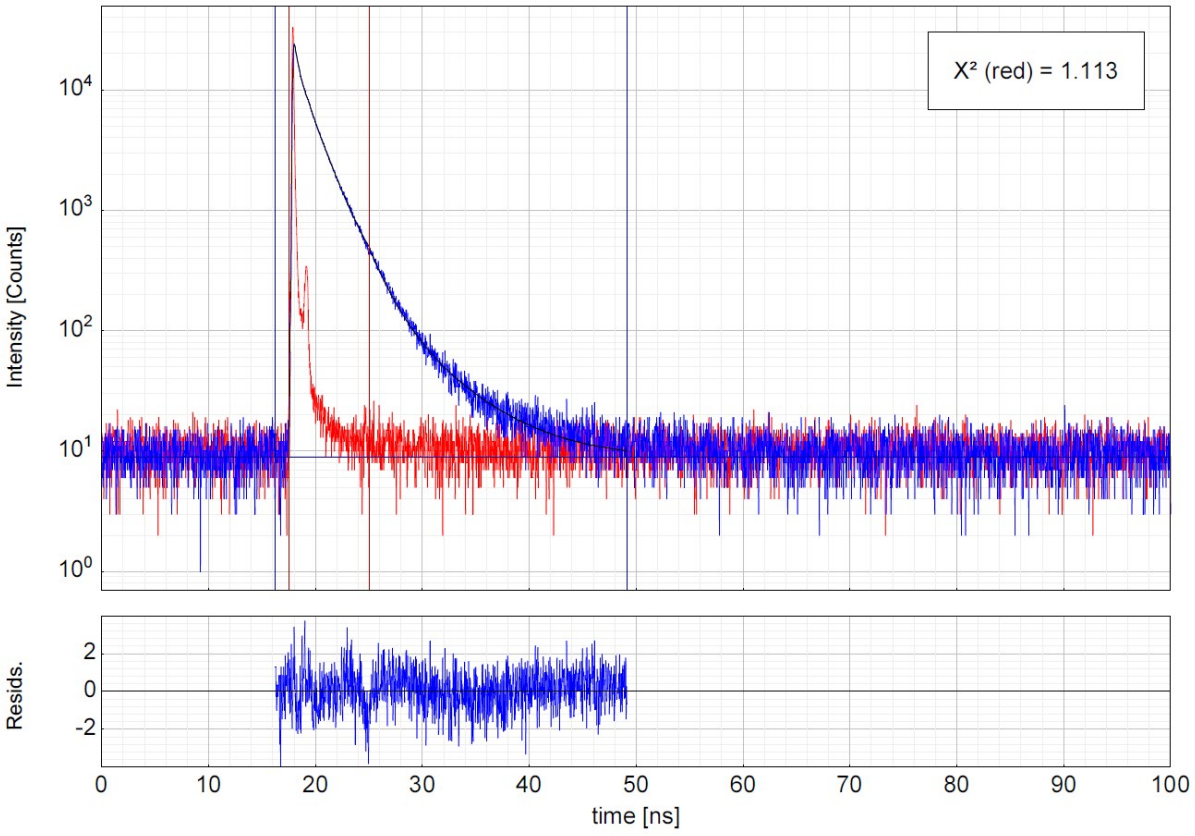


Figure S3. Quantum yield determination for **H_3.L** (+ O_2) in 0.1 M HEPES buffer at pH 7.4 at room temperature.



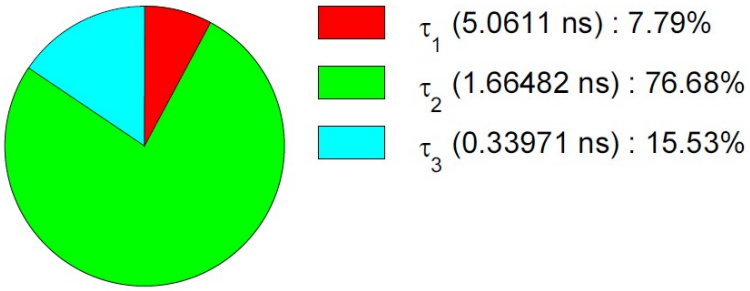
Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A_1 [Cnts]	662	-184	+184	Fitting
τ_1 [ns]	5.0611	-0.0587	+0.0761	Support Plane
A_2 [Cnts]	19832	-900	+900	Fitting
τ_2 [ns]	1.66482	-0.00726	+0.00875	Support Plane
A_3 [Cnts]	19680	-3290	+3290	Fitting
τ_3 [ns]	0.33971	-0.00444	+0.00552	Support Plane
Bkgr. Dec [Cnts]	8.85	-6.47	+6.47	Fitting
Bkgr. IRF [Cnts]	-6.0	-14.6	+14.6	Fitting
Shift IRF [ns]	-0.007802	-0.000295	+0.000295	Fitting
A Scat [Cnts]	3360	-18200	+18200	Fitting

Average Lifetime:

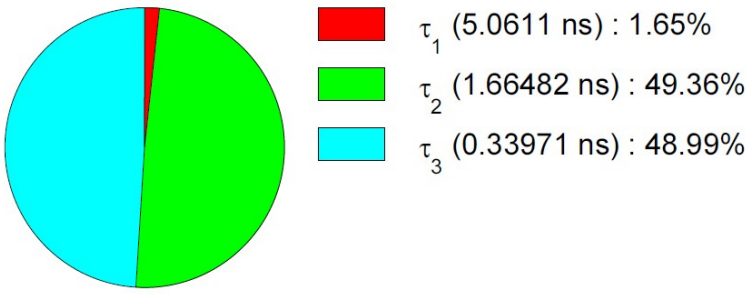
$\tau_{Av.1}$=1.7235 ns (intensity weighted)

$\tau_{Av.2}$=1.0716 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:



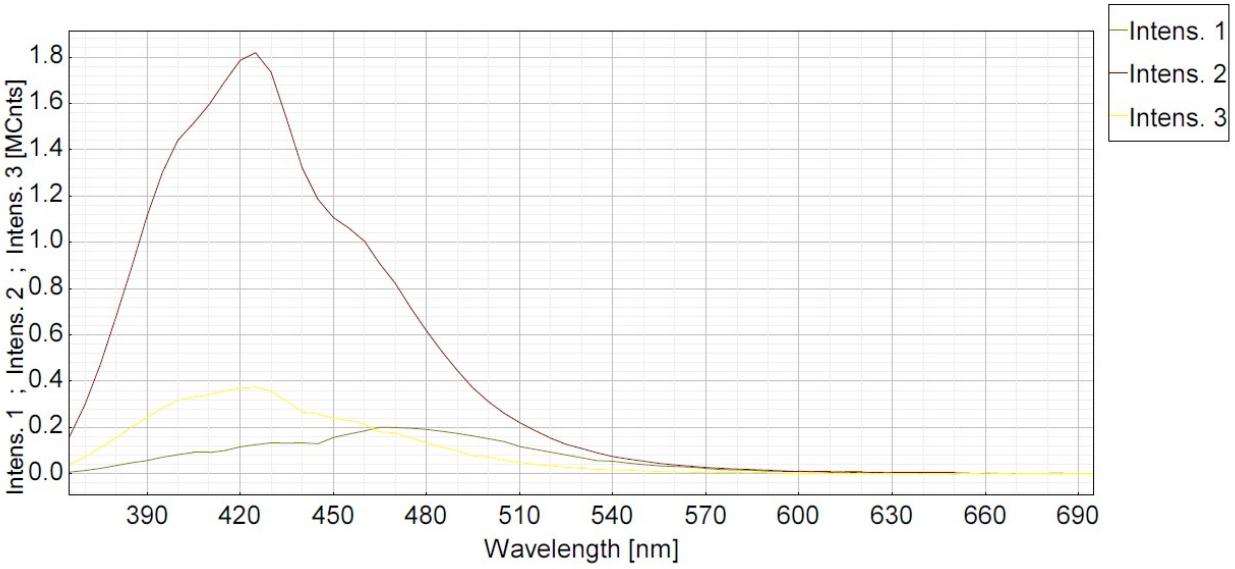
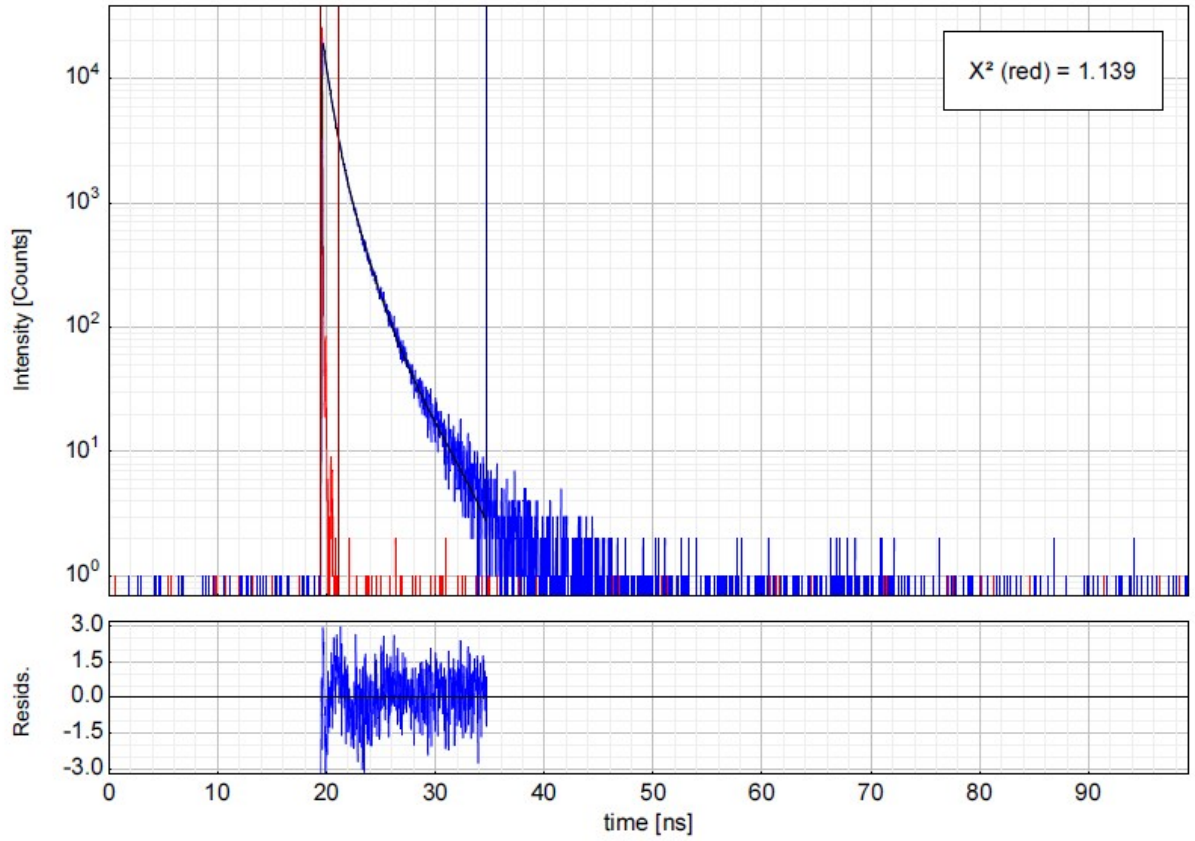


Figure S4. Fluorescence decay profile observed for **H_3.L** (-O_2) in HEPES Buffer pH 7.4. Top, time-resolved emission decay profile. Middle, result of global fit from time resolved emission spectra. Bottom, emission spectra deconvoluted using three lifetime components. The data was fitted to a triexponential decay to determine the associated lifetimes.



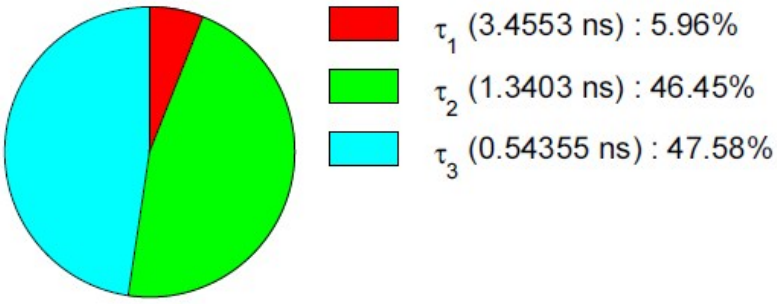
Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A_1 [Cnts]	318.7	-93.3	+93.3	Fitting
τ_1 [ns]	3.4553	-0.0481	+0.0597	Support Plane
A_2 [Cnts]	6400	-424	+424	Fitting
τ_2 [ns]	1.3403	-0.0115	+0.0250	Support Plane
A_3 [Cnts]	16163	-1000	+1000	Fitting
τ_3 [ns]	0.54355	-0.00377	+0.00662	Support Plane
Bkgr. Dec [Cnts]	-1.40	-5.28	+5.28	Fitting
Bkgr. IRF [Cnts]	-9.8	-25.8	+25.8	Fitting
Shift IRF [ns]	0.62766	-0.00685	+0.00685	Fitting
A Scat [Cnts]	-14740	-4480	+4480	Fitting

Average Lifetime:

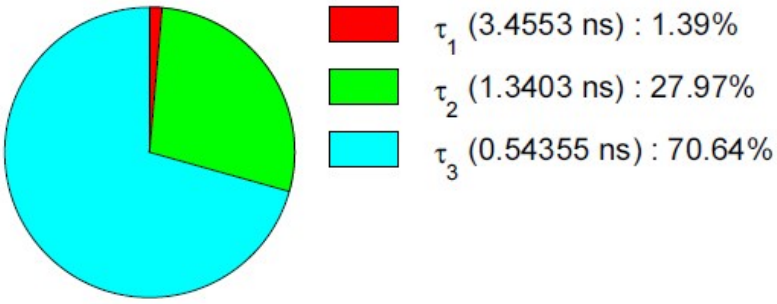
$\tau_{Av.1}$=1.0873 ns (intensity weighted)

$\tau_{Av.2}$=0.8070 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:



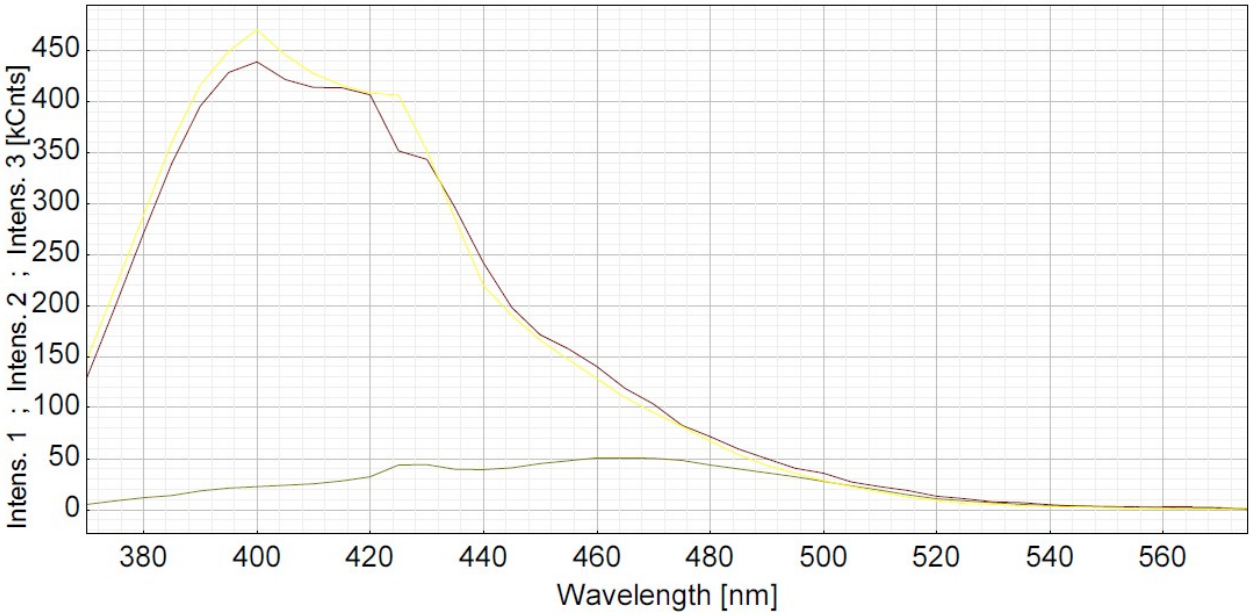


Figure S5. Fluorescence decay profile observed for **H_3.L** (+ O_2) in HEPES Buffer pH 7.4. Top, time-resolved emission decay profile. Middle, result of global fit from time resolved emission spectra. Bottom, emission spectra deconvoluted using three lifetime components. The data was fitted to a triexponential decay to determine the associated lifetimes.

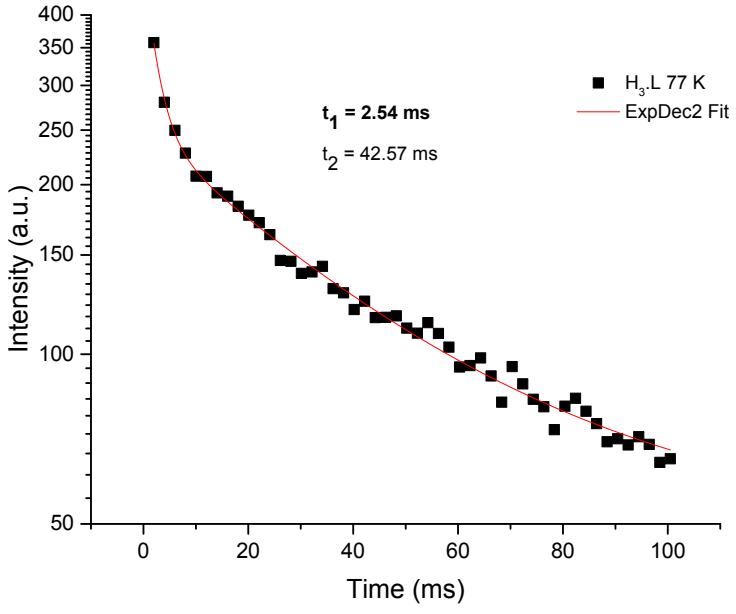


Figure S6. Time-resolved emission decay profile and fit for **H_3.L** at 77 K in HEPES buffer pH 7.4, monitored at 500 nm following 325 nm light excitation, Gate time 0.2 ms, Delay 2 ms, Total decay time 100 ms.

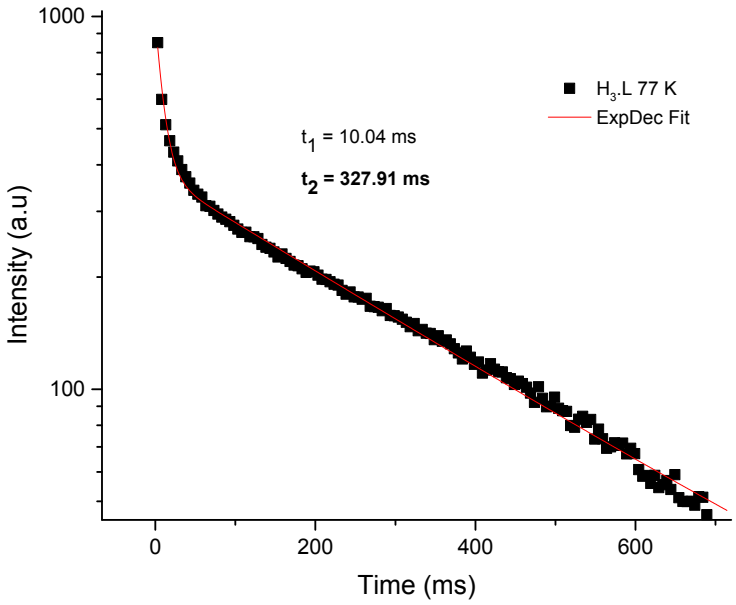


Figure S7. Time-resolved emission decay profile and fit for **H_3.L** at 77 K in HEPES buffer pH 7.4, monitored at 500 nm following 325 nm light excitation, Gate time 0.5 ms, Delay 5 ms, Total decay time 800 ms.

Optical Spectroscopy: $\underline{H_5.L^{+2}}$

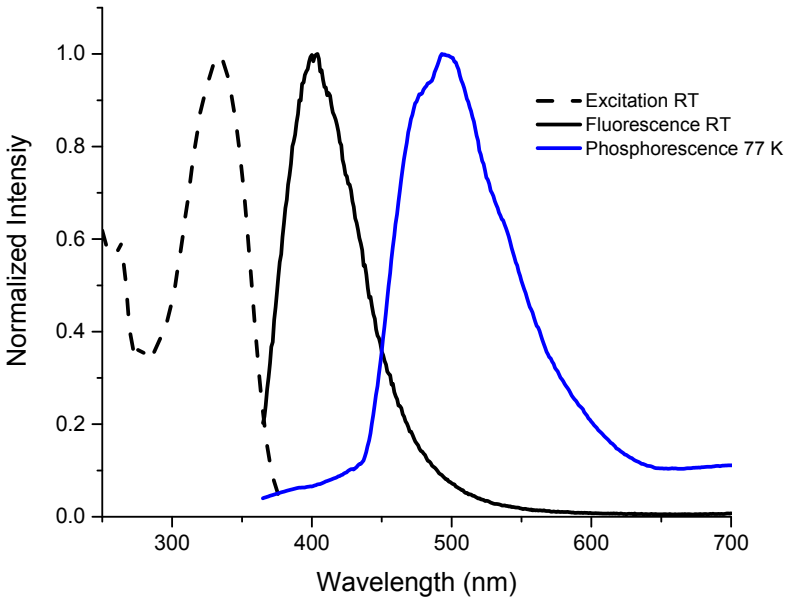


Figure S8. Excitation (followed at 402 nm) and emission (excitation 355 nm) spectra of a $1.14 \cdot 10^{-5}$ M solution of $\mathbf{H_5.L^{2+}}$ in HEPES buffer at pH 7.4 at room temperature. Phosphorescence spectrum of the same solution at 77 K, Gate time 1 ms, Delay 5 ms.

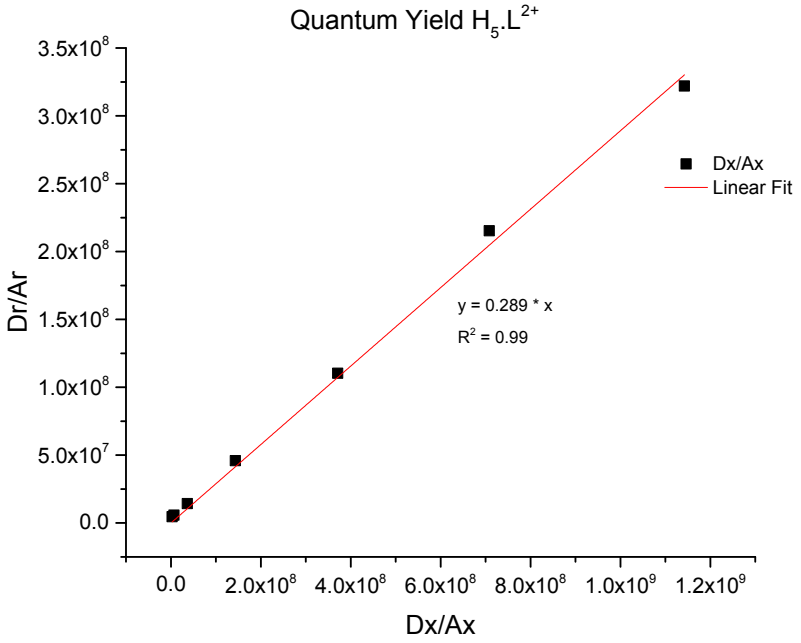


Figure S9. Quantum yield determination for $\mathbf{H_5.L^{2+}}$ (- O_2) in 0.1 M HEPES buffer at pH 7.4 at room temperature.

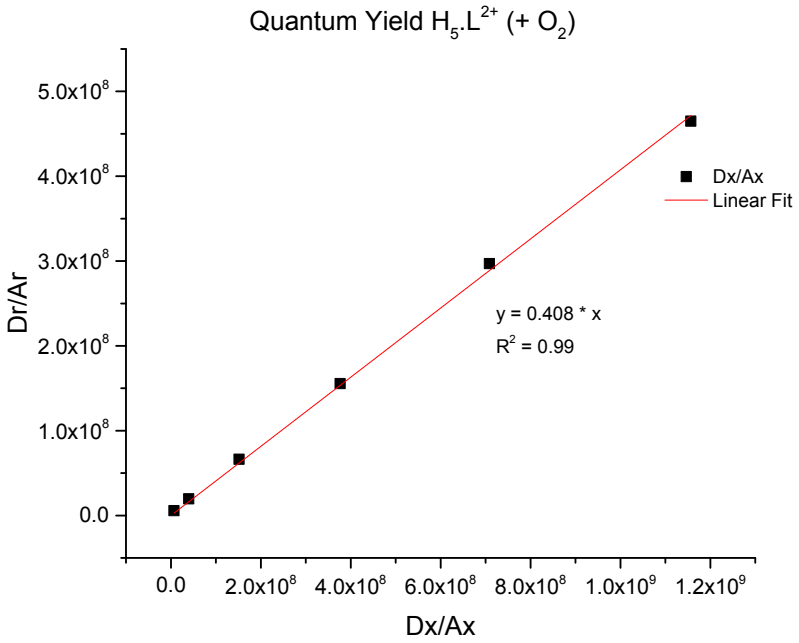
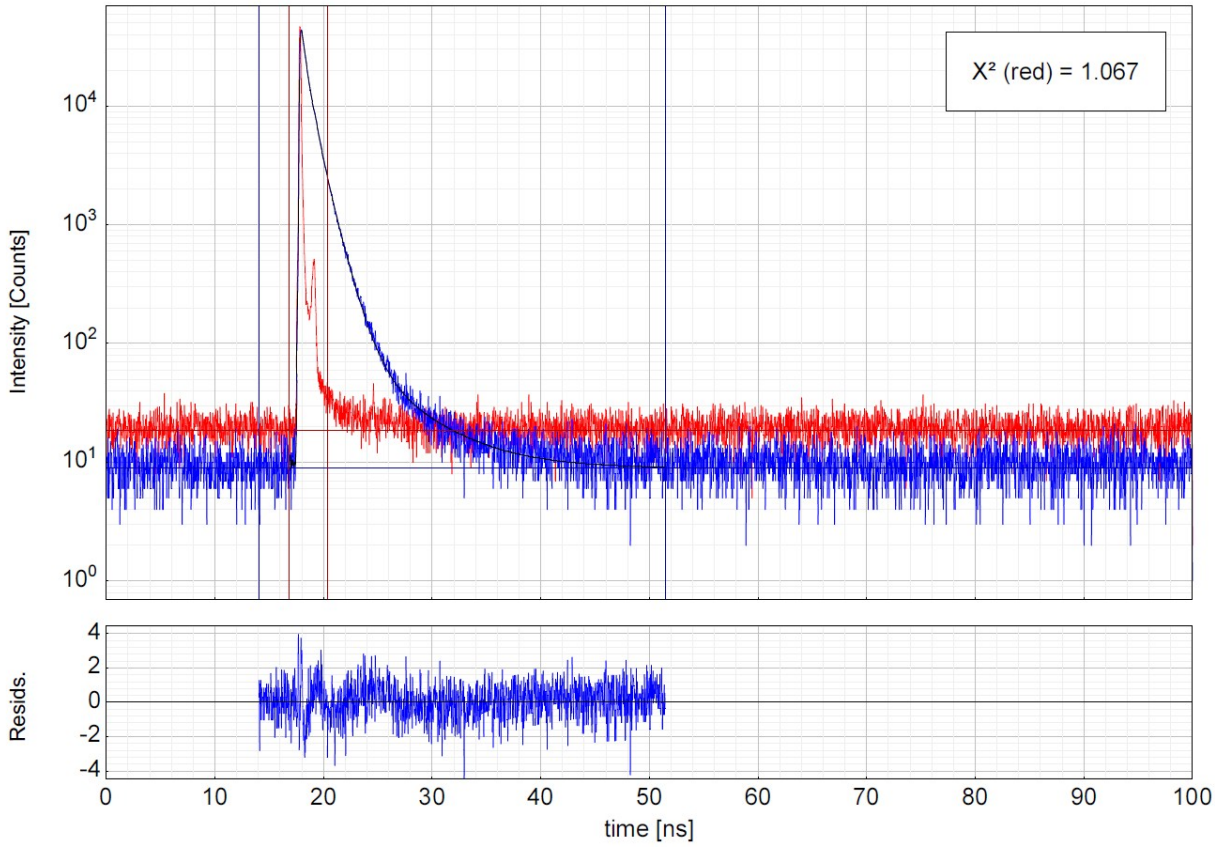


Figure S10. Quantum yield determination for **$H_5.L^{2+}$** (+ O_2) in 0.1 M HEPES buffer at pH 7.4 at room temperature.



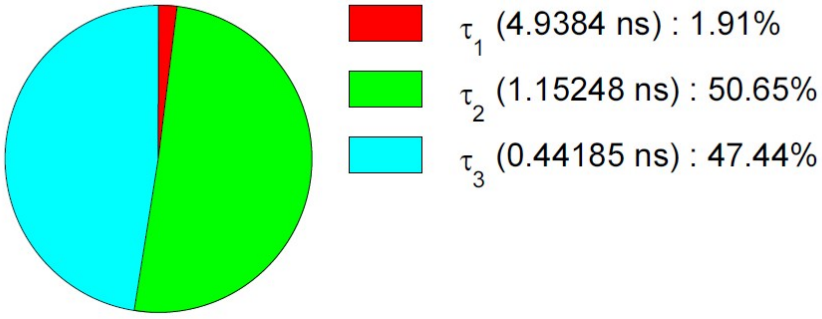
Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A_1 [Cnts]	201	-144	+144	Fitting
τ_1 [ns]	4.9384	-0.0085	+0.0994	Bootstrap
A_2 [Cnts]	22840	-1790	+1790	Fitting
τ_2 [ns]	1.15248	-0.00198	+0.01262	Bootstrap
A_3 [Cnts]	55780	-4640	+4640	Fitting
τ_3 [ns]	0.44185	-0.00166	+0.00711	Bootstrap
Bkgr. Dec [Cnts]	8.92	-6.00	+6.00	Fitting
Bkgr. IRF [Cnts]	18.7	-17.8	+17.8	Fitting
Shift IRF [ns]	-0.00266	-0.0104	+0.0104	Fitting
A Scat [Cnts]	13800	-33100	+33100	Fitting

Average Lifetime:

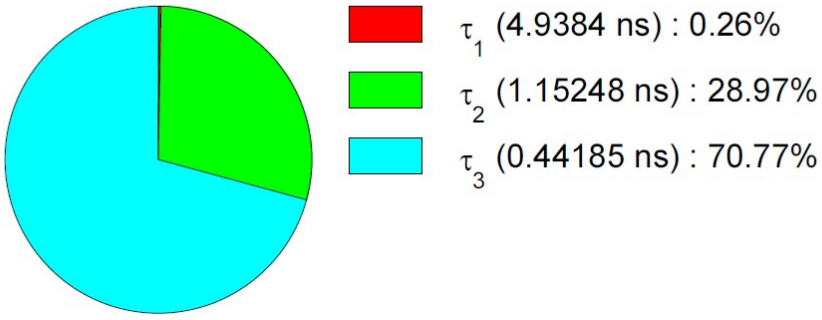
$\tau_{Av.1}$=0.8879 ns (intensity weighted)

$\tau_{Av.2}$=0.6592 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:



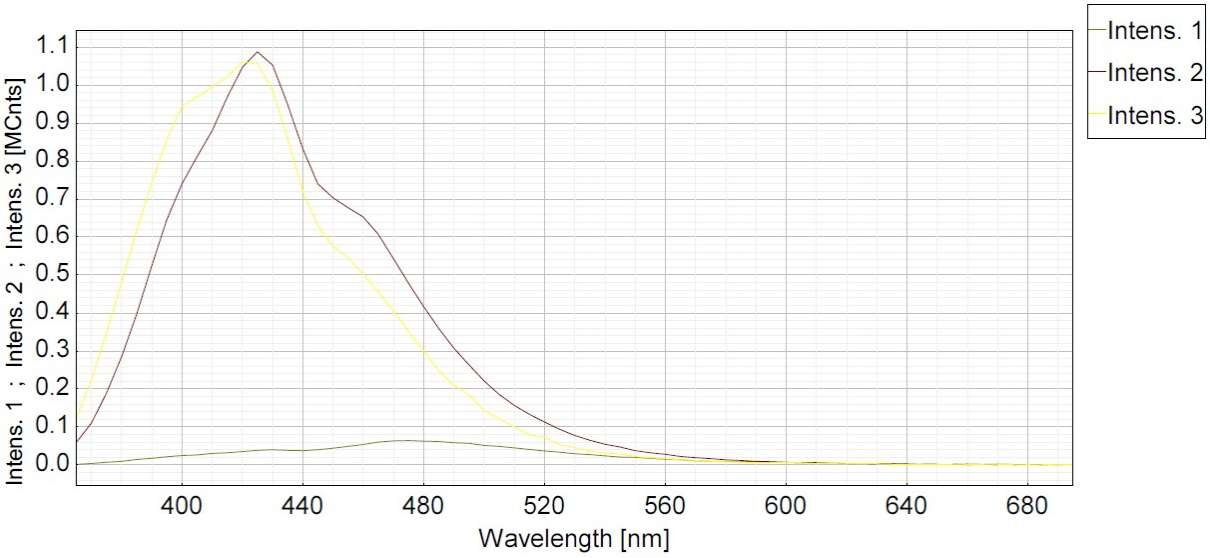
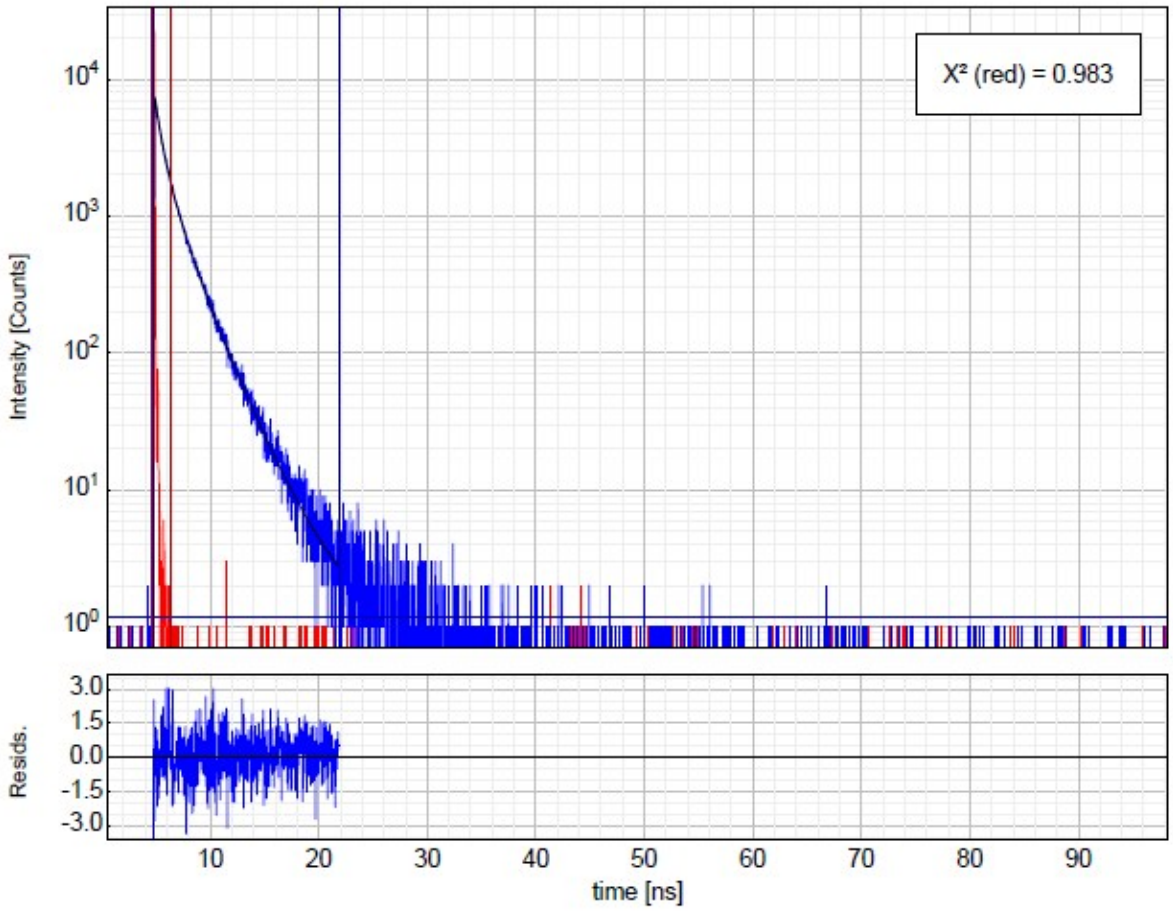


Figure S11. Fluorescence decay profile observed for $\mathbf{H_5.L^{2+}}$ ($-O_2$) in HEPES Buffer pH 7.4. Top, time-resolved emission decay profile. Middle, result of global fit from time resolved emission spectra. Bottom, emission spectra deconvoluted using three lifetime components. The data was fitted to a triexponential decay to determine the associated lifetimes.



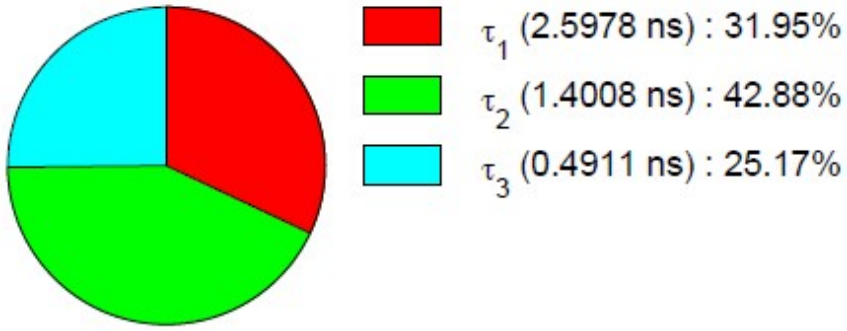
Parameter	Value	Conf. $_{Lower}$	Conf. $_{Upper}$	Conf. $_{Estimation}$
A_1 [Cnts]	1086	-126	+126	Fitting
τ_1 [ns]	2.5978	-0.1163	+0.0523	Support Plane
A_2 [Cnts]	2702	-262	+262	Fitting
τ_2 [ns]	1.4008	-0.1445	+0.0397	Support Plane
A_3 [Cnts]	4524	-627	+627	Fitting
τ_3 [ns]	0.4911	-0.0217	+0.0071	Support Plane
Bkgr. $_{Dec}$ [Cnts]	1.16	-4.19	+4.19	Fitting
Bkgr. $_{IRF}$ [Cnts]	-21.4	-36.4	+36.4	Fitting
Shift $_{IRF}$ [ns]	-0.00901	-0.00746	+0.00746	Fitting
A $_{Scat}$ [Cnts]	2300	-3590	+3590	Fitting

Average Lifetime:

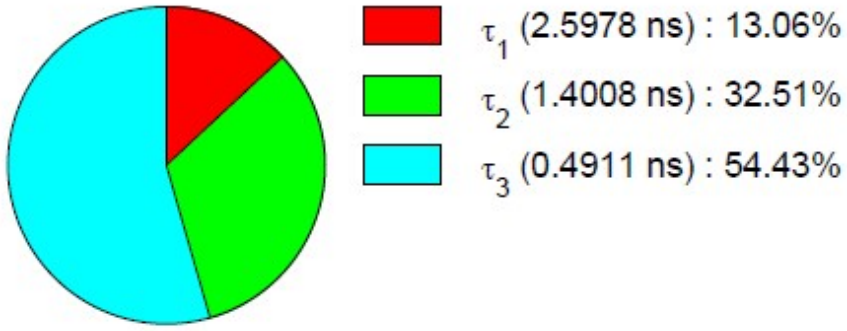
$\tau_{Av.1}$=1.5544 ns (intensity weighted)

$\tau_{Av.2}$=1.0620 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:



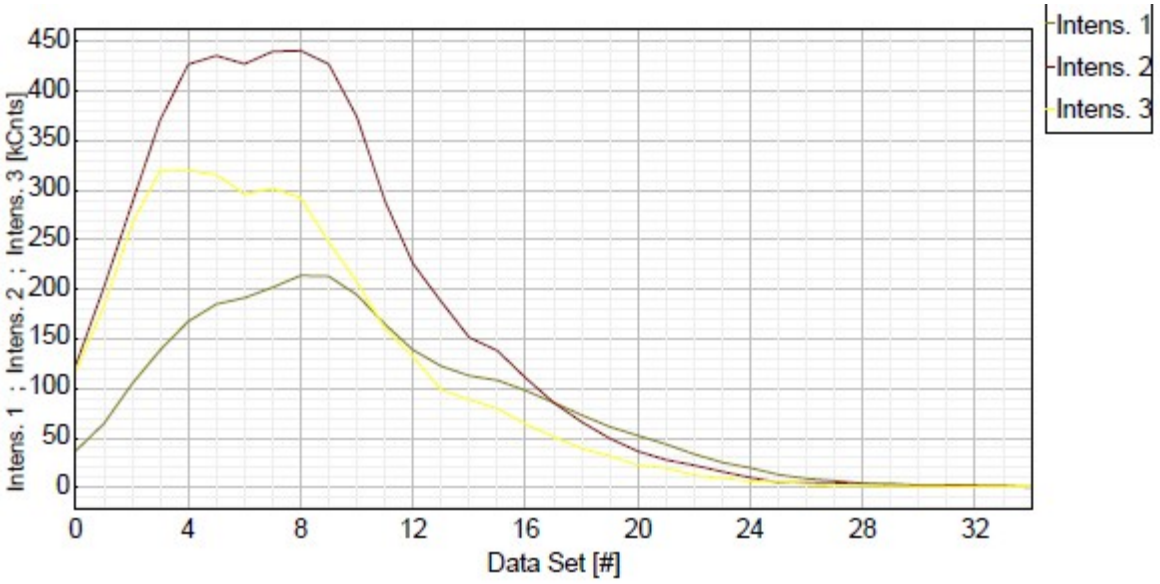


Figure S12. Fluorescence decay profile observed for $\mathbf{H_5.L^{2+}}$ (+ O_2) in HEPES Buffer pH 7.4. Top, time-resolved emission decay profile. Middle, result of global fit from time resolved emission spectra. Bottom, emission spectra deconvoluted using three lifetime components. The data was fitted to a triexponential decay to determine the associated lifetimes.

Optical Spectroscopy: Eu.L

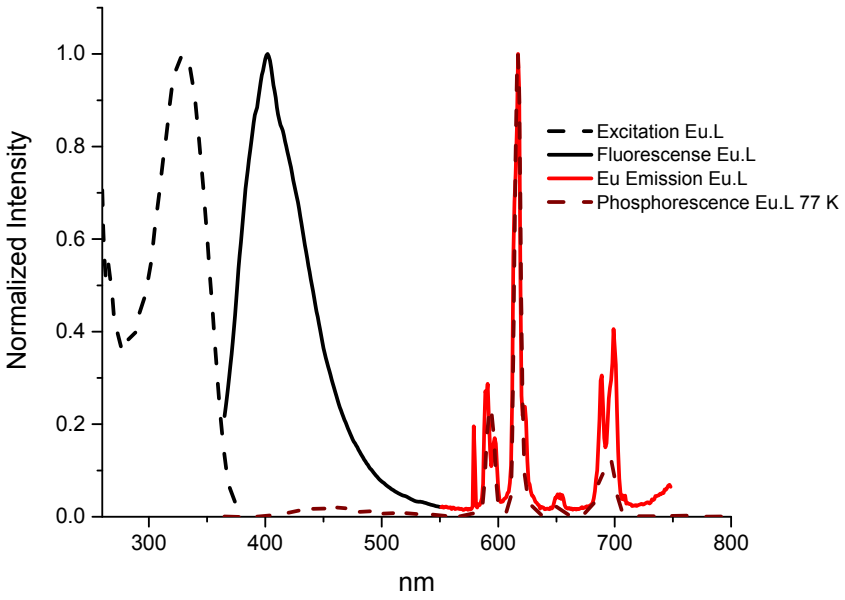


Figure S13. Excitation (followed at 402 nm) and emission (excitation 355 nm) spectra of a 1.14 $\cdot 10^{-5}$ M solution of **Eu.L** in HEPES buffer at pH 7.4 at room temperature. Phosphorescence spectrum of the same solution at 77 K, Gate time 1 ms, Delay 5 ms.

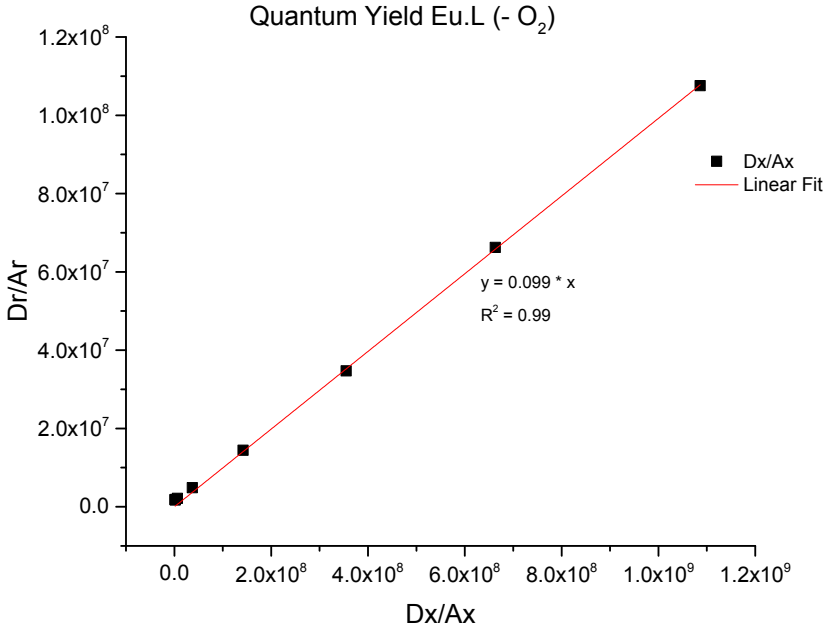


Figure S14. Quantum yield determination for **Eu.L** (- O_2) in 0.1 M HEPES buffer at pH 7.4 at room temperature.

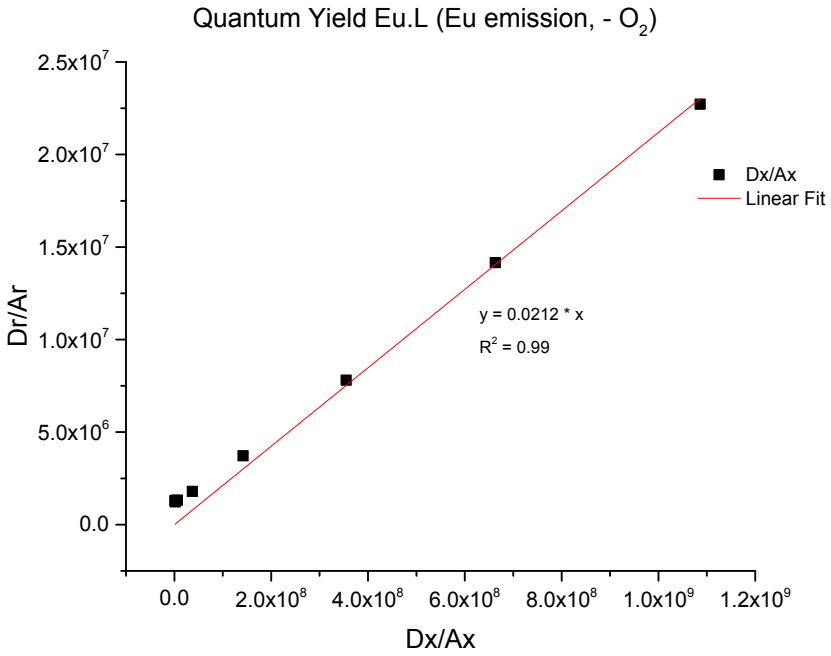


Figure S15. Quantum yield determination for **Eu.L** (Eu emission, - O_2) in 0.1 M HEPES buffer at pH 7.4 at room temperature.

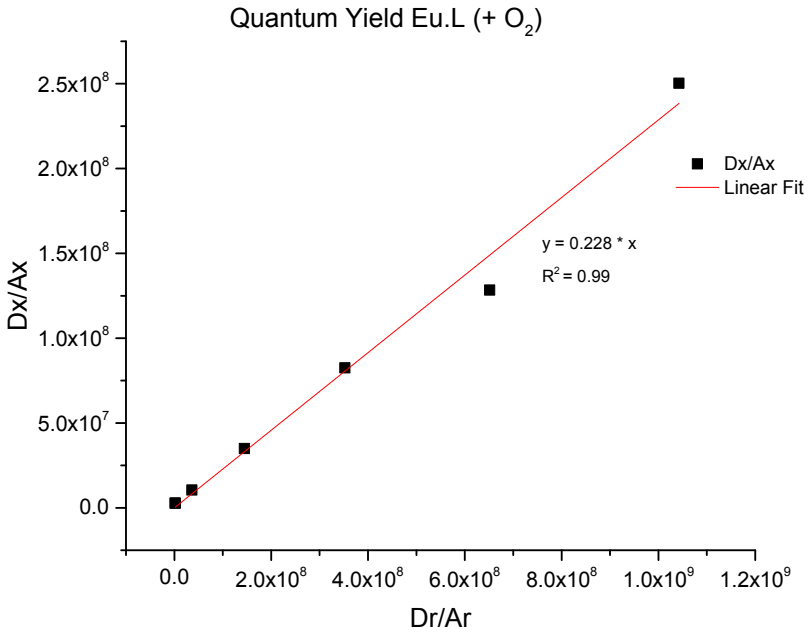
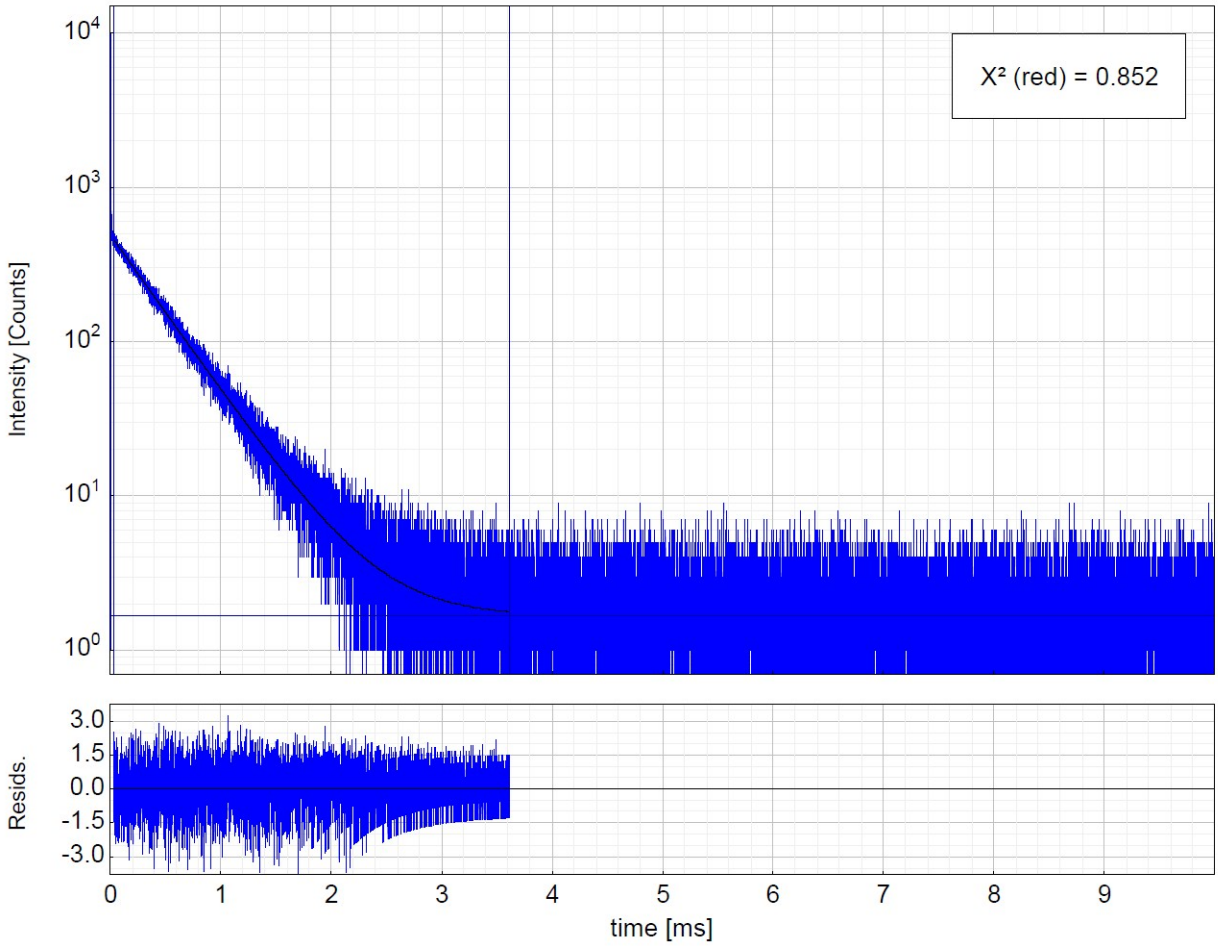


Figure S16. Quantum yield determination for **Eu.L** (+ O_2) in 0.1 M HEPES buffer at pH 7.4 at room temperature.



Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A_1 [Cnts]	455.78	-9.18	+9.18	Fitting
τ_1 [ms]	0.42881	-0.00126	+0.00124	Support Plane
Bkgr. Dec [Cnts]	1.668	-0.401	+0.401	Fitting

Average Lifetime:

$\tau_{Av.1}$=0.42881 ms (intensity weighted)

$\tau_{Av.2}$=0.42881 ms (amplitude weighted)

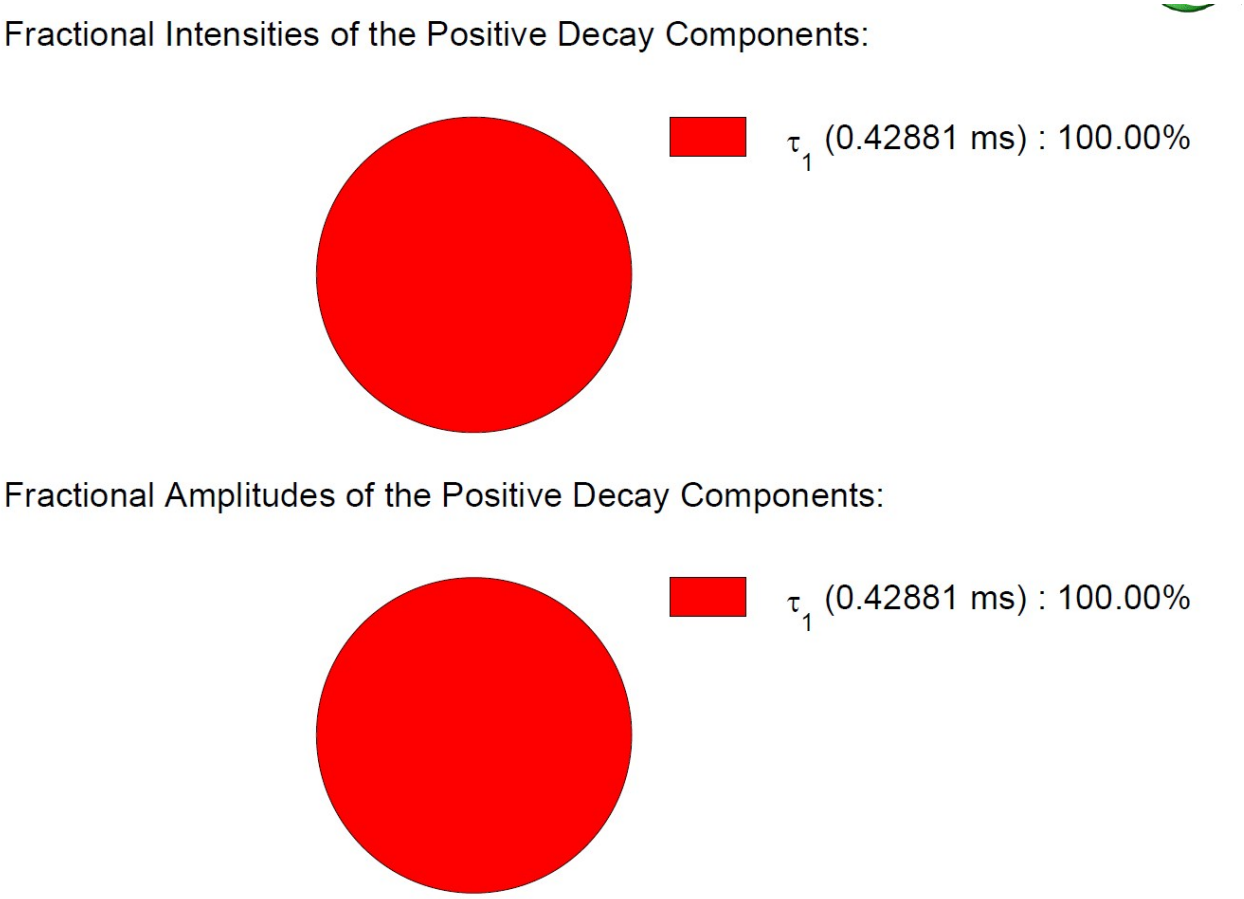
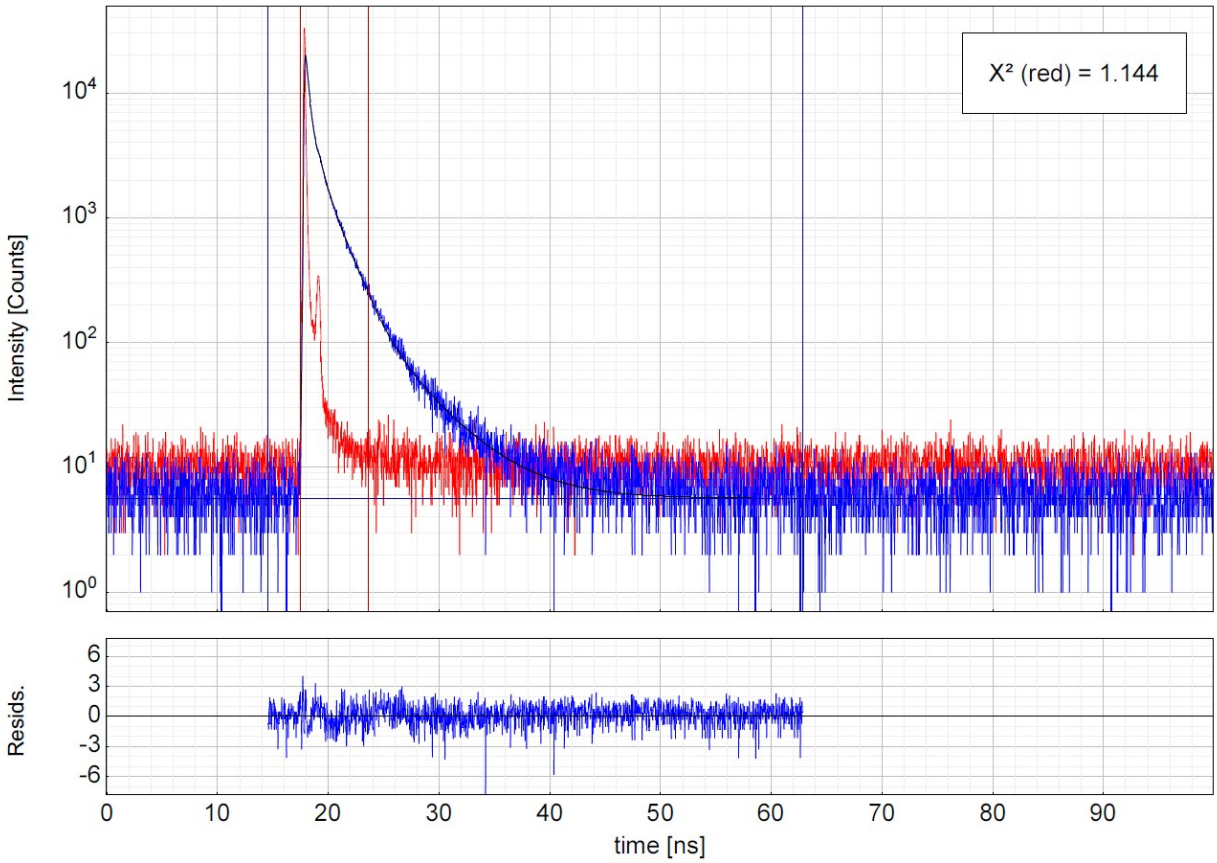


Figure S17. Luminescence decay profile observed for **Eu.L** (-O_2) in HEPES Buffer pH 7.4. Excitation 355 nm, emission followed at 616 nm. The data was fitted to a single exponential decay to determine the associated lifetime of the metal centred luminescence.



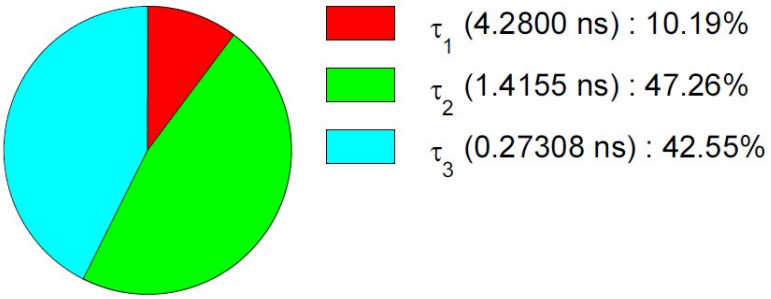
Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A_1 [Cnts]	502	-196	+196	Fitting
τ_1 [ns]	4.2800	-0.0432	+0.0736	Support Plane
A_2 [Cnts]	7045	-902	+902	Fitting
τ_2 [ns]	1.4155	-0.0095	+0.0130	Support Plane
A_3 [Cnts]	32880	-4370	+4370	Fitting
τ_3 [ns]	0.27308	-0.00126	+0.00179	Support Plane
Bkgr. $_{Dec}$ [Cnts]	5.65	-4.48	+4.48	Fitting
Bkgr. $_{IRF}$ [Cnts]	-0.257	-33.8	+33.8	Fitting
Shift $_{IRF}$ [ns]	-0.0491	-0.0166	+0.0166	Fitting

Average Lifetime:

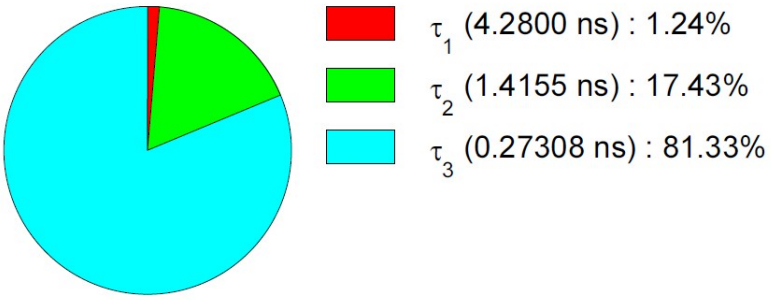
$\tau_{Av.1}$=1.2211 ns (intensity weighted)

$\tau_{Av.2}$=0.5219 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:



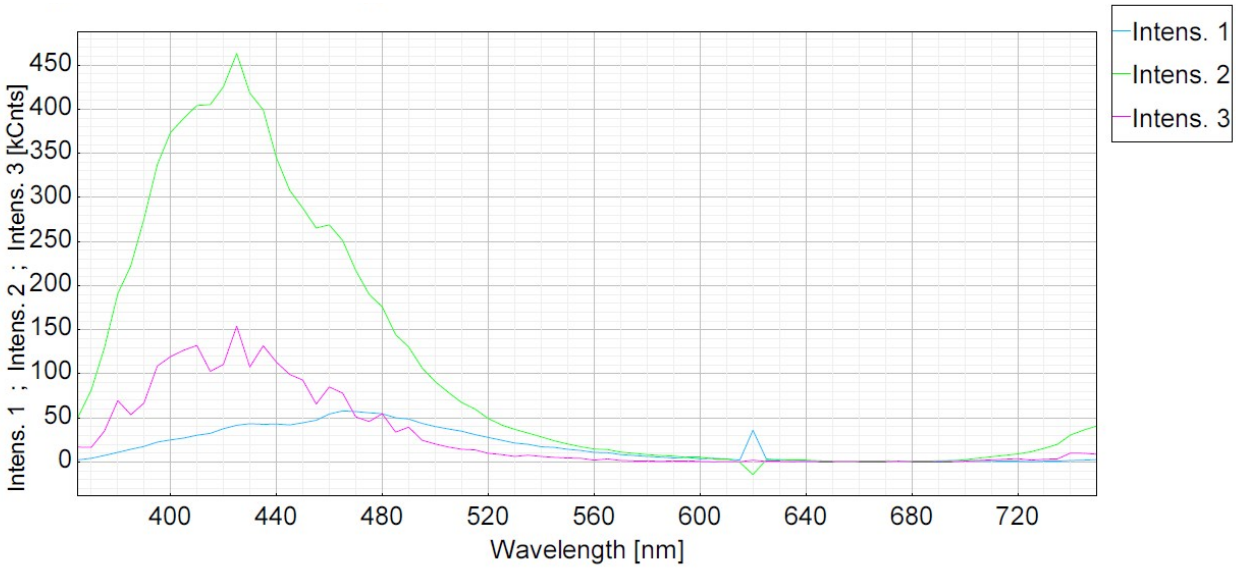
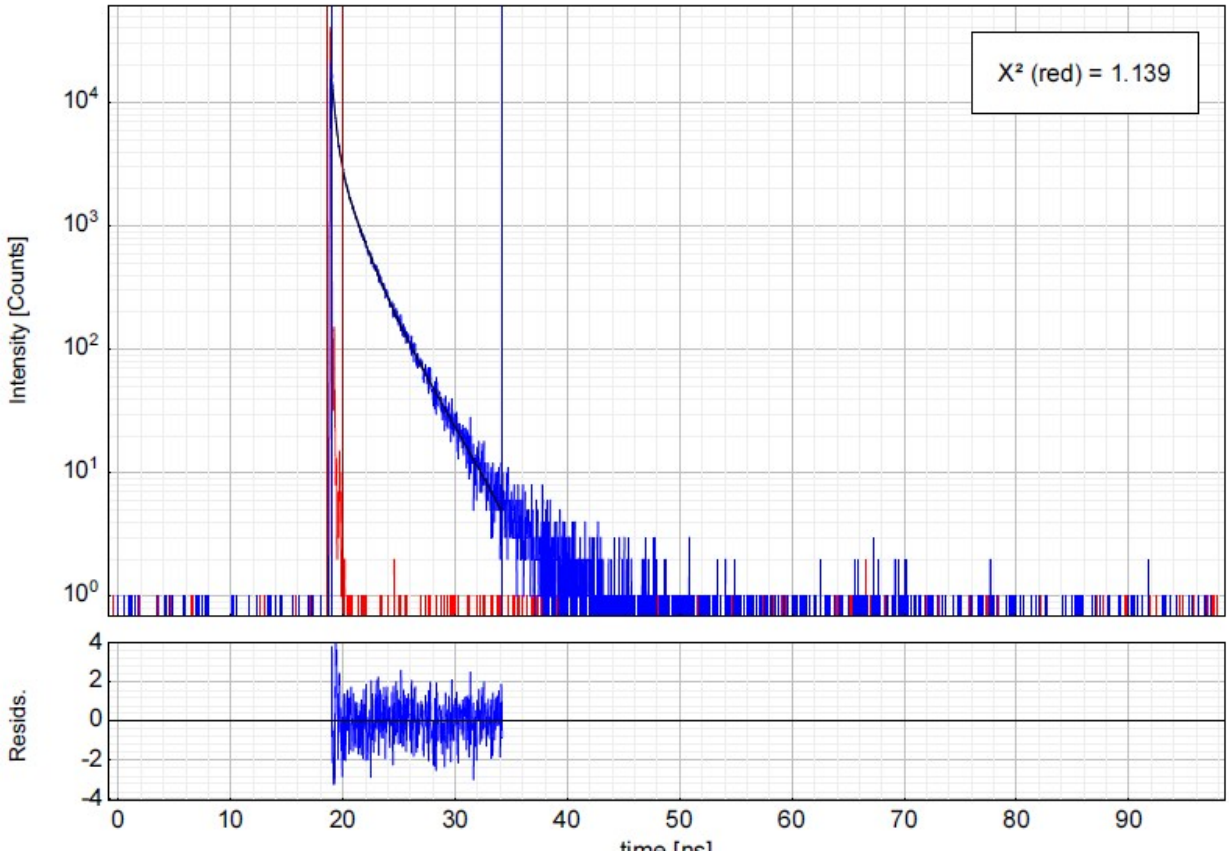


Figure S18. Fluorescence decay profile observed for **Eu.L** (-O_2) in HEPES Buffer pH 7.4. Top, time-resolved emission decay profile. Middle, result of global fit from time resolved emission spectra. Bottom,

emission spectra deconvoluted using three lifetime components. The data was fitted to a triexponential decay to determine the associated lifetimes.



Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A_1 [Cnts]	977	-153	+153	Fitting
τ_1 [ns]	2.9402	-0.0223	+0.0296	Support Plane
A_2 [Cnts]	3696	-431	+431	Fitting
τ_2 [ns]	1.3156	-0.0094	+0.0128	Support Plane
A_3 [Cnts]	20320	-2330	+2330	Fitting
τ_3 [ns]	0.26714	-0.00096	+0.00159	Support Plane
Bkgr. Dec [Cnts]	-0.96	-8.19	+8.19	Fitting
Bkgr. IRF [Cnts]	-126.3	-89.7	+89.7	Fitting
Shift IRF [ns]	-0.9193	-0.0250	+0.0250	Fitting
A Scat [Cnts]	56000	-208000	+208000	Fitting

Average Lifetime:

$\tau_{Av.1}$=1.2378 ns (intensity weighted)

$\tau_{Av.2}$=0.5267 ns (amplitude weighted)

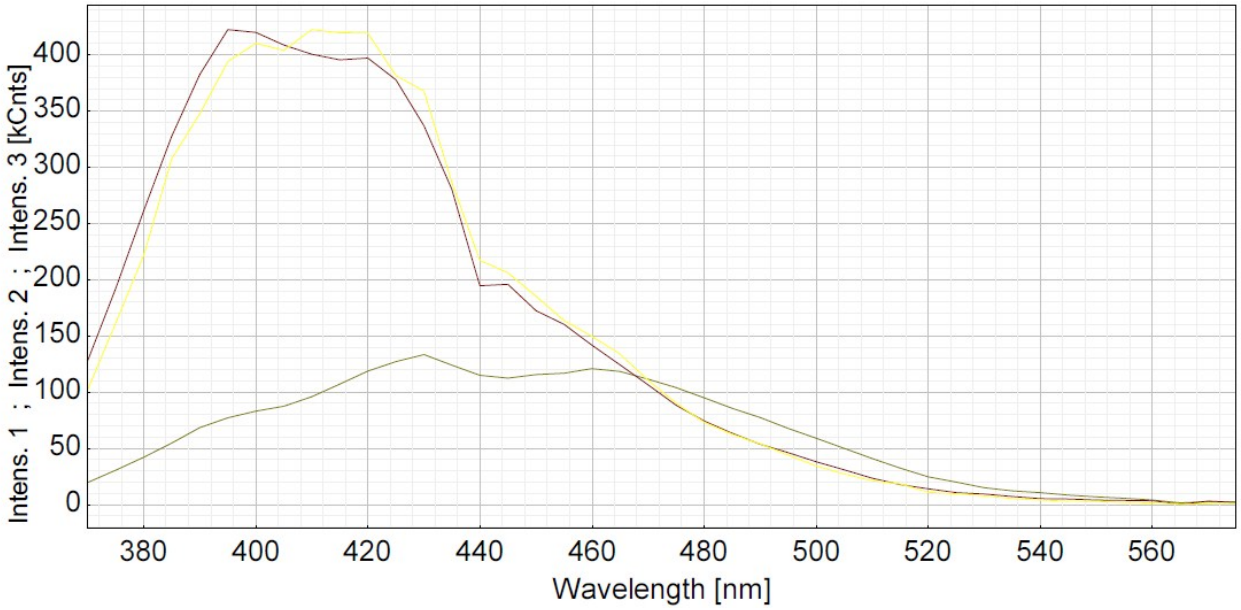


Figure S19. Fluorescence decay profile observed for **Eu.L** (+O_2) in HEPES Buffer pH 7.4. Top, time-resolved emission decay profile. Middle, result of global fit from time resolved emission spectra. Bottom, emission spectra deconvoluted using three lifetime components. The data was fitted to a triexponential decay to determine the associated lifetimes.

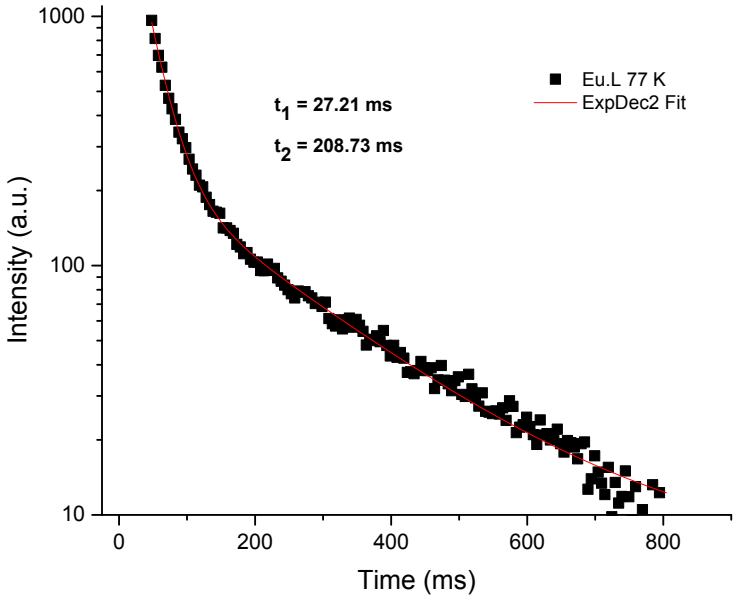


Figure S20. Time-resolved emission decay profile and fit for **Eu.L** at 77 K in HEPES buffer pH 7.4, monitored at 450 nm following 325 nm light excitation, Gate time 0.5 ms, Delay 5 ms, Total decay time 800 ms.

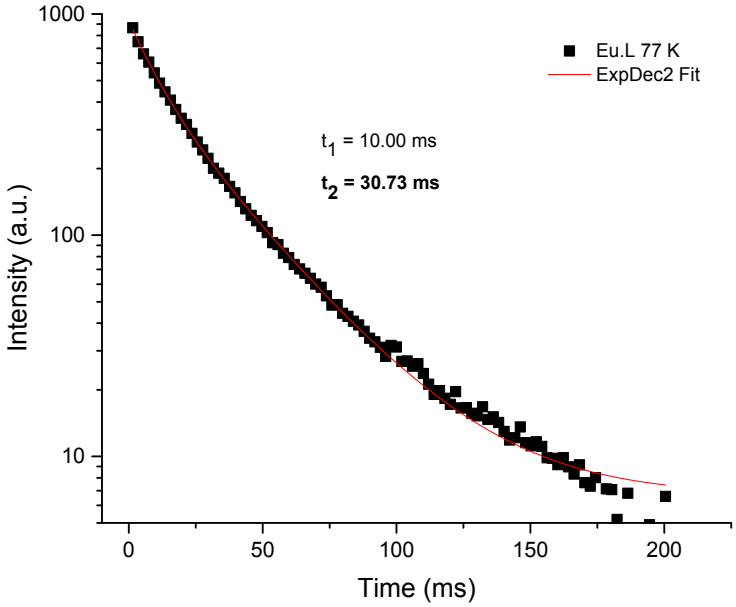


Figure S21. Time-resolved emission decay profile and fit for **Eu.L** at 77 K in HEPES buffer pH 7.4, monitored at 450 nm following 325 nm light excitation, Gate time 0.5 ms, Delay 2 ms, Total decay time 200 ms.

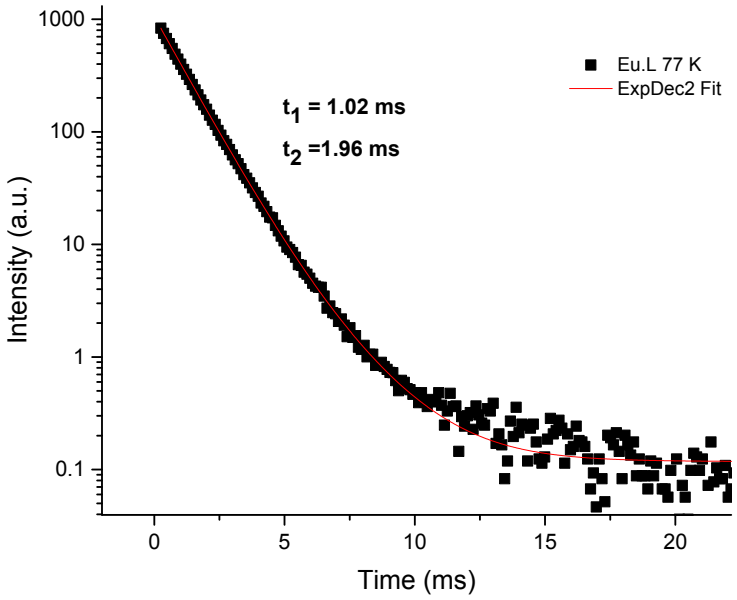


Figure S22. Time-resolved emission decay profile and fit for **Eu.L** at 77 K in HEPES buffer pH 7.4, monitored at 690 nm following 325 nm light excitation, Gate time 0.1 ms, Delay 0.2 ms, Total decay time 100 ms.

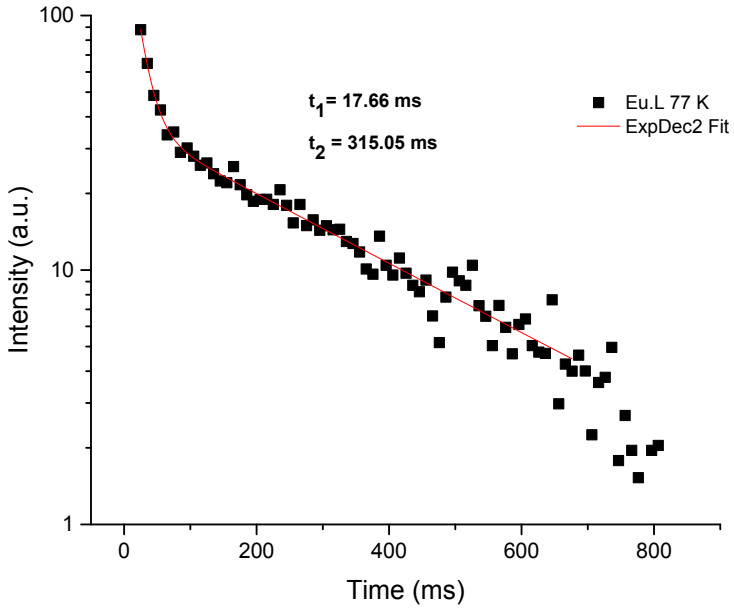


Figure S23. Time-resolved emission decay profile and fit for **Eu.L** at 77 K in HEPES buffer pH 7.4, monitored at 616 nm following 325 nm light excitation, Gate time 20 ms, Delay 5 ms, Total decay time 800 ms.

Optical Spectroscopy: Gd.L

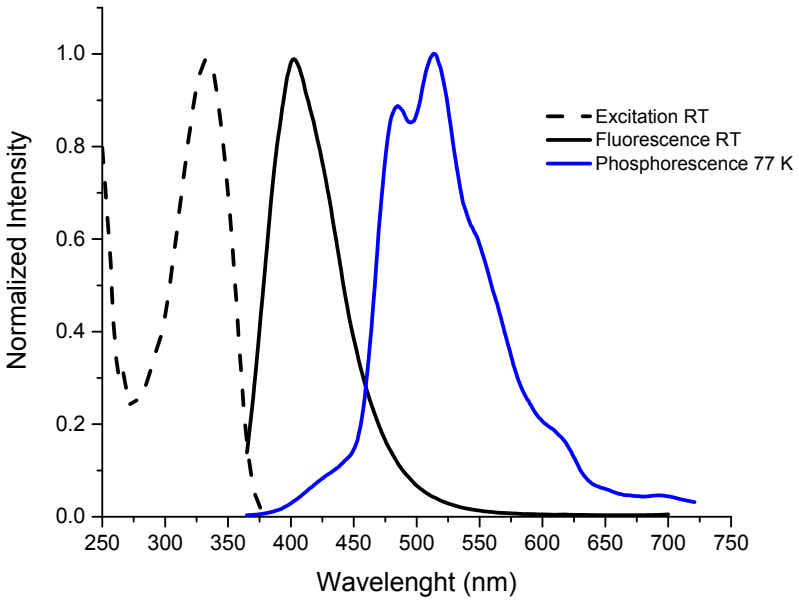


Figure S24. Excitation (followed at 402 nm) and emission (excitation 355 nm) spectra of a 1.14 $\cdot 10^{-5}$ M solution of **Gd.L** in HEPES buffer at pH 7.4 at room temperature. Phosphorescence spectrum of the same solution at 77 K, Gate time 1 ms, Delay 5 ms.

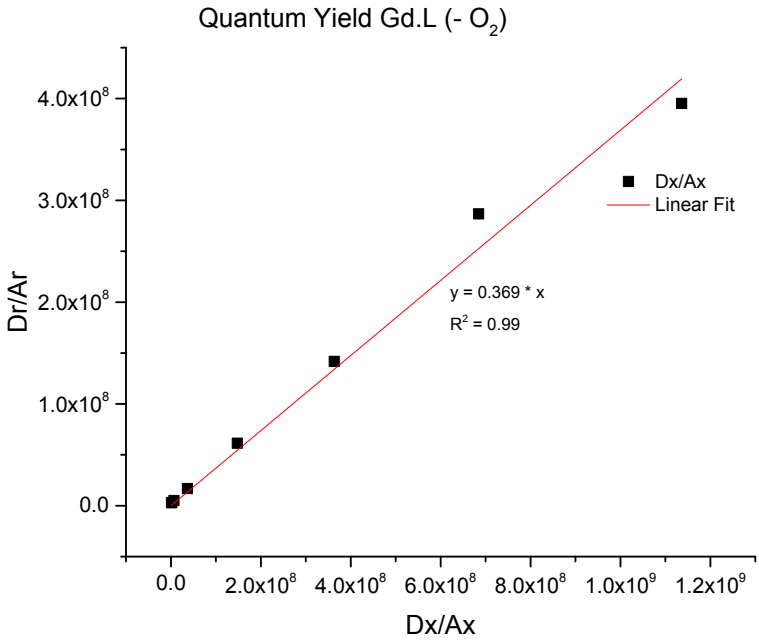


Figure S25. Quantum yield determination for **Gd.L** (- O_2) in 0.1 M HEPES buffer at pH 7.4 at room temperature.

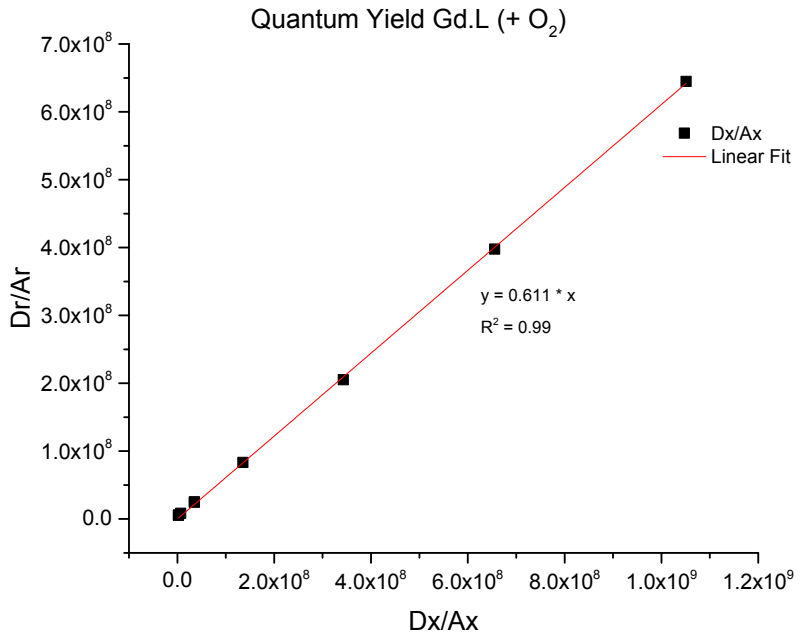
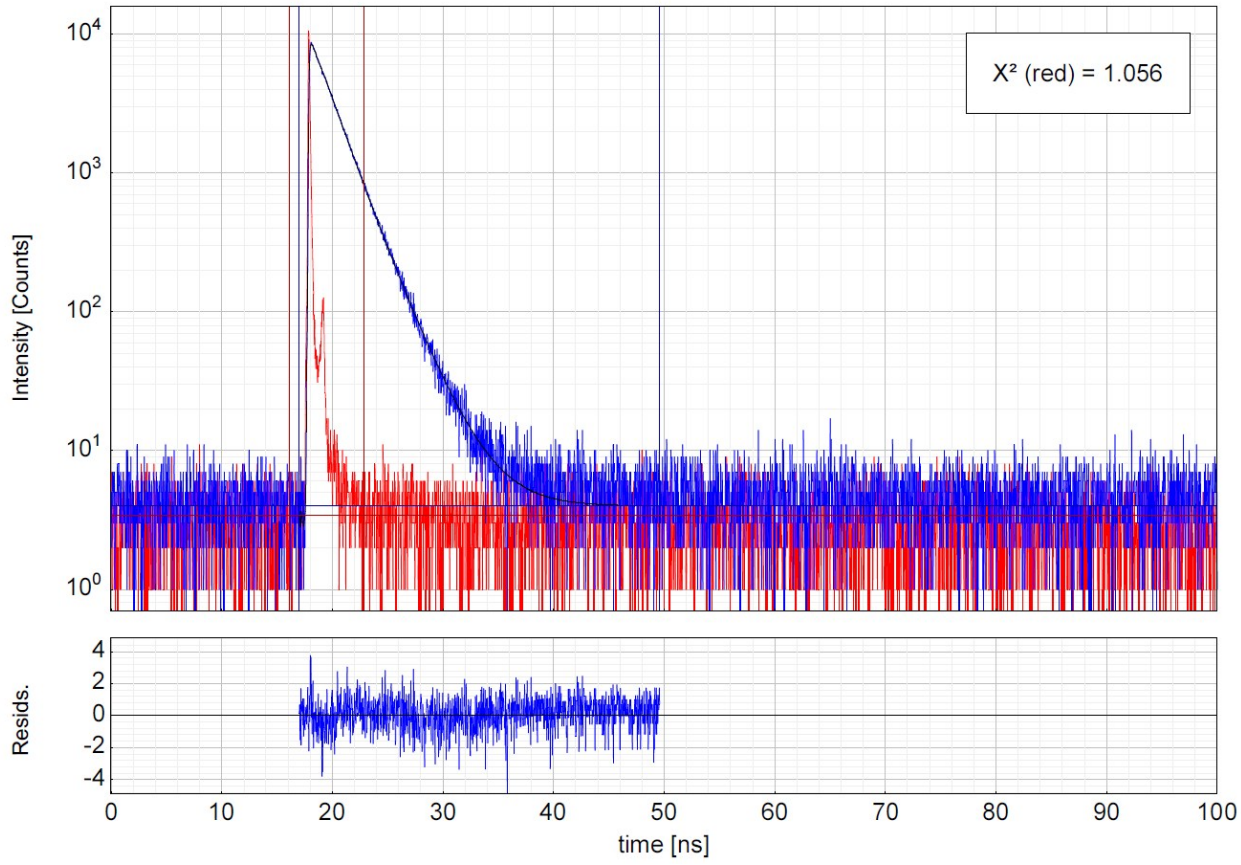


Figure S26. Quantum yield determination for **Gd.L** (+ O_2) in 0.1 M HEPES buffer at pH 7.4 at room temperature.



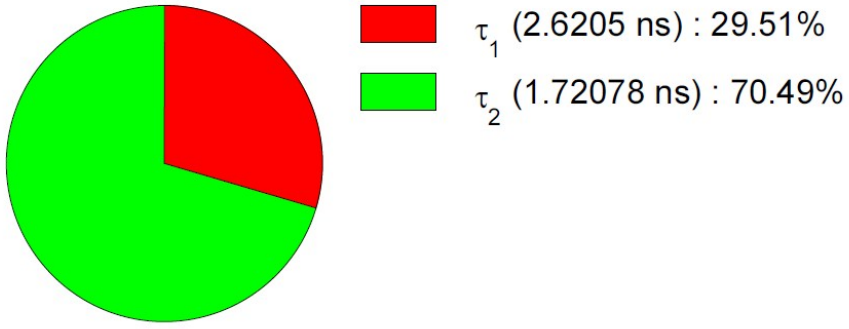
Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A_1 [Cnts]	2619	-522	+522	Fitting
τ_1 [ns]	2.6205	-0.00254	+0.0198	Bootstrap
A_2 [Cnts]	9527	-810	+810	Fitting
τ_2 [ns]	1.72078	-0.000274	+0.00961	Bootstrap
Bkgr. Dec [Cnts]	3.99	-5.11	+5.11	Fitting
Bkgr. IRF [Cnts]	3.41	-4.58	+4.58	Fitting
Shift IRF [ns]	-0.0401	-0.0248	+0.0248	Fitting
A Scat [Cnts]	-13600	-9330	+9330	Fitting

Average Lifetime:

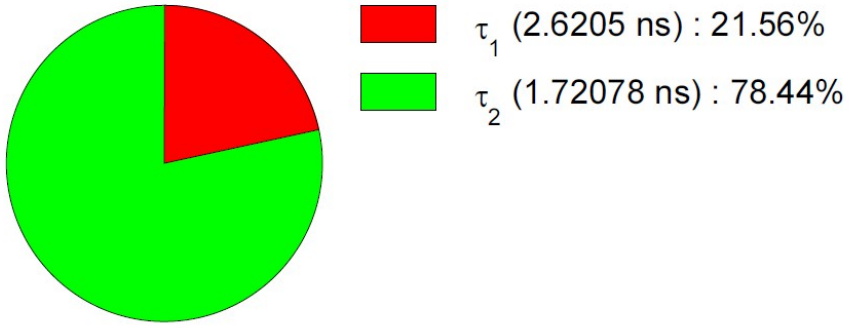
$\tau_{Av.1}$=1.9863 ns (intensity weighted)

$\tau_{Av.2}$=1.9148 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:



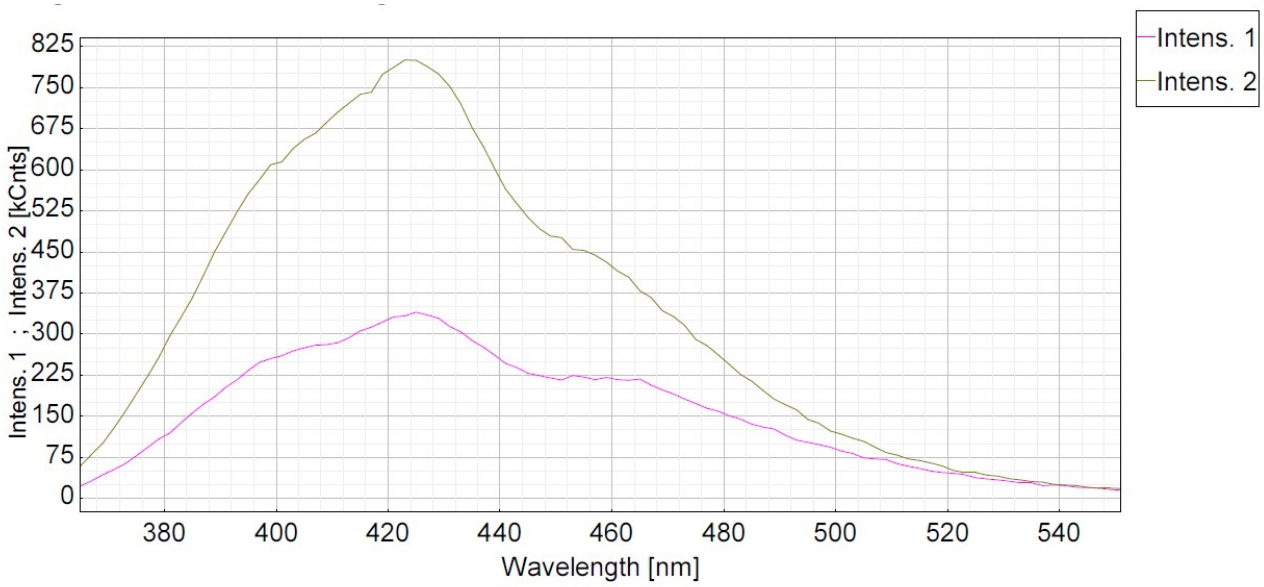
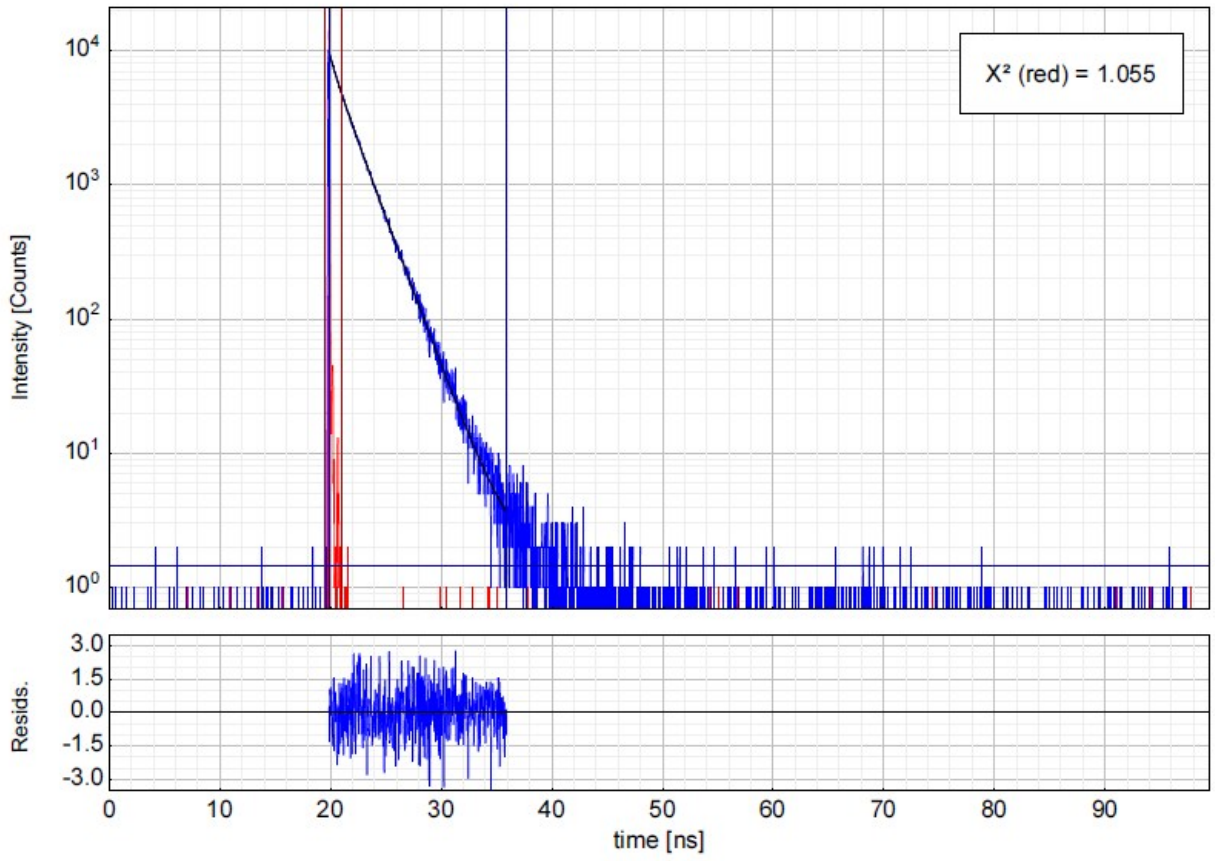


Figure S27. Fluorescence decay profile observed for **Gd.L** (-O_2) in HEPES Buffer pH 7.4. Top, time-resolved emission decay profile. Middle, result of global fit from time resolved emission spectra. Bottom, emission spectra deconvoluted using two lifetime components. The data was fitted to a biexponential decay to determine the associated lifetimes.



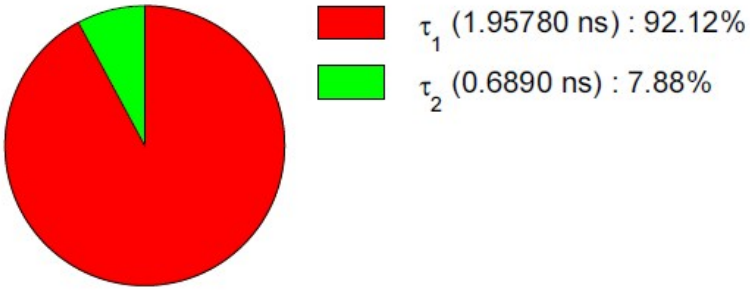
Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A_1 [Cnts]	8043	-306	+306	Fitting
τ_1 [ns]	1.95780	-0.00305	+0.00623	Support Plane
A_2 [Cnts]	1955	-715	+715	Fitting
τ_2 [ns]	0.6890	-0.0138	+0.0328	Support Plane
Bkgr. Dec [Cnts]	1.44	-6.01	+6.01	Fitting
Bkgr. IRF [Cnts]	-1.47	-23.3	+23.3	Fitting
Shift IRF [ns]	0.3043	-0.0339	+0.0339	Fitting
A Scat [Cnts]	8060	-9920	+9920	Fitting

Average Lifetime:

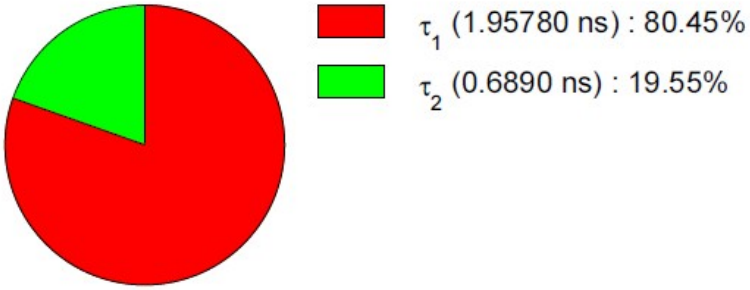
$\tau_{Av.1}$=1.85782 ns (intensity weighted)

$\tau_{Av.2}$=1.70970 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:



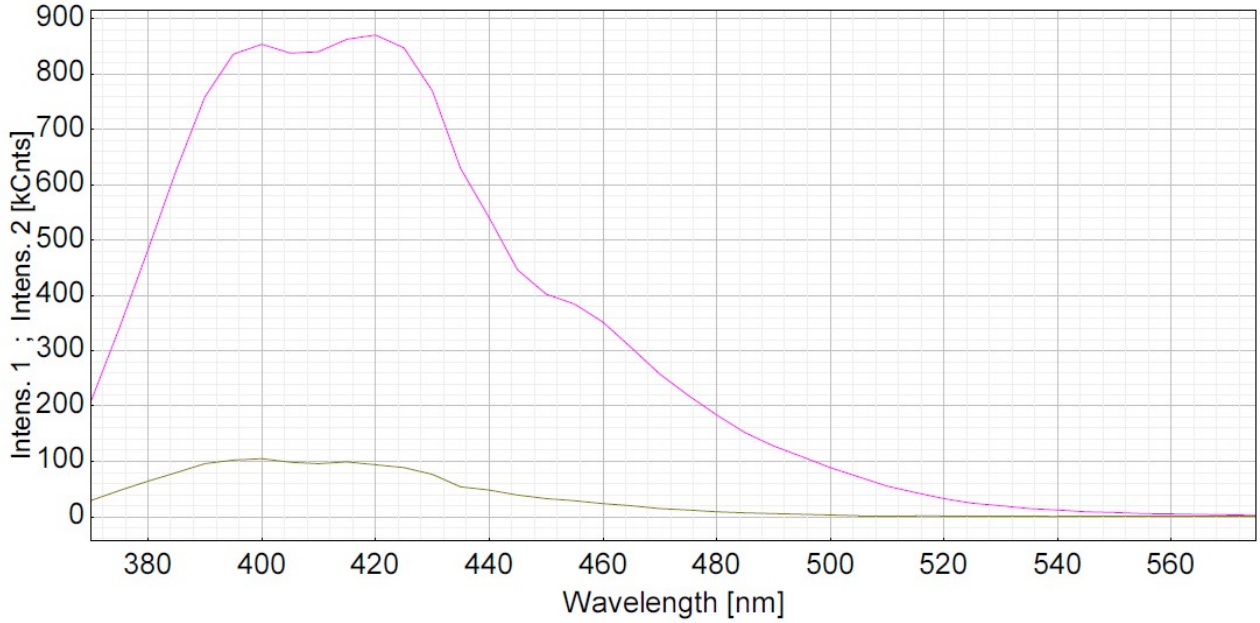


Figure S28. Fluorescence decay profile observed for **Gd.L** (+O_2) in HEPES Buffer pH 7.4. Top, time-resolved emission decay profile. Middle, result of global fit from time resolved emission spectra. Bottom, emission spectra deconvoluted using two lifetime components. The data was fitted to a biexponential decay to determine the associated lifetimes.

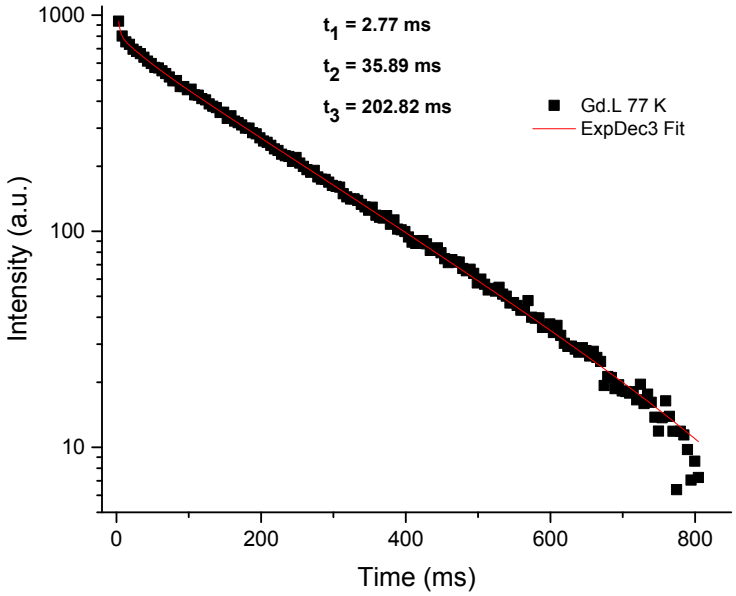


Figure S29. Time-resolved emission decay profile and fit for **Gd.L** at 77 K in HEPES buffer pH 7.4, monitored at 500 nm following 325 nm light excitation, Gate time 0.5 ms, Delay 5 ms, Total decay time 800 ms.

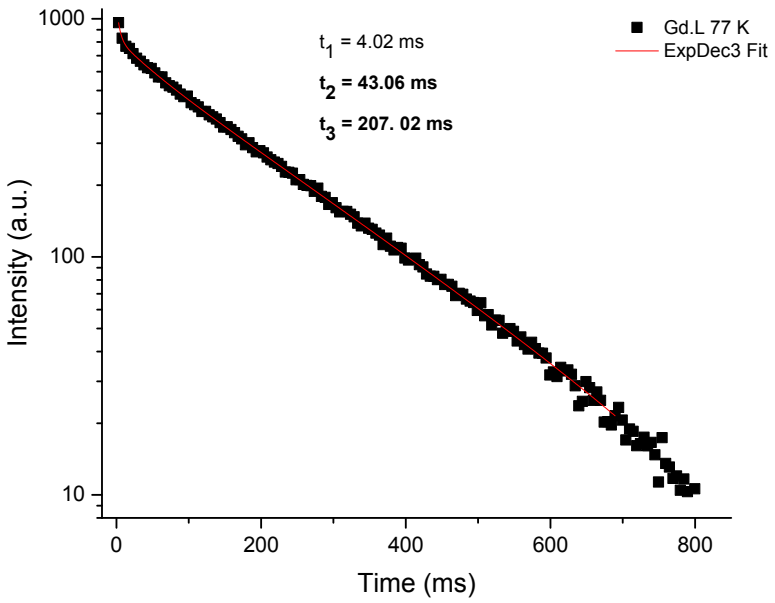


Figure S30. Time-resolved emission decay profile and fit for **Gd.L** at 77 K in HEPES buffer pH 7.4, monitored at 500 nm following 325 nm light excitation, Gate time 0.5 ms, Delay 5 ms, Total decay time 800 ms.

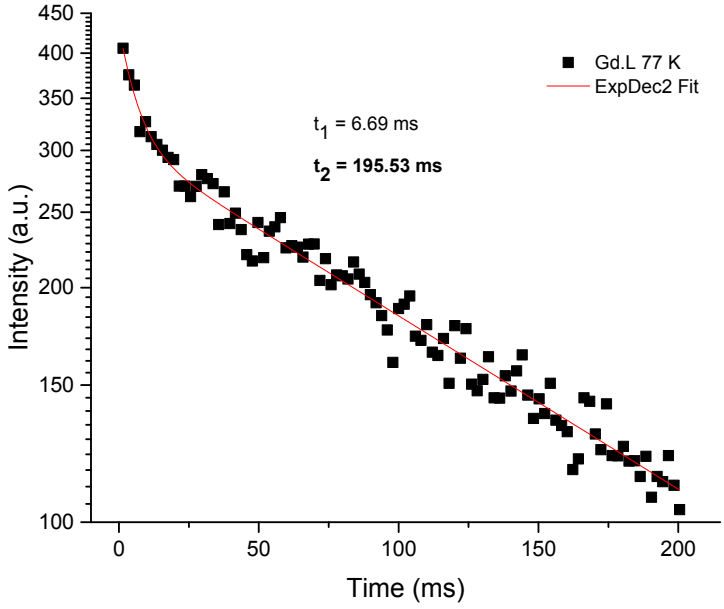


Figure S31. Time-resolved emission decay profile and fit for **Gd.L** at 77 K in HEPES buffer pH 7.4, monitored at 500 nm following 325 nm light excitation, Gate time 0.2 ms, Delay 2 ms, Total decay time 200 ms.

Optical Spectroscopy: Tb.L

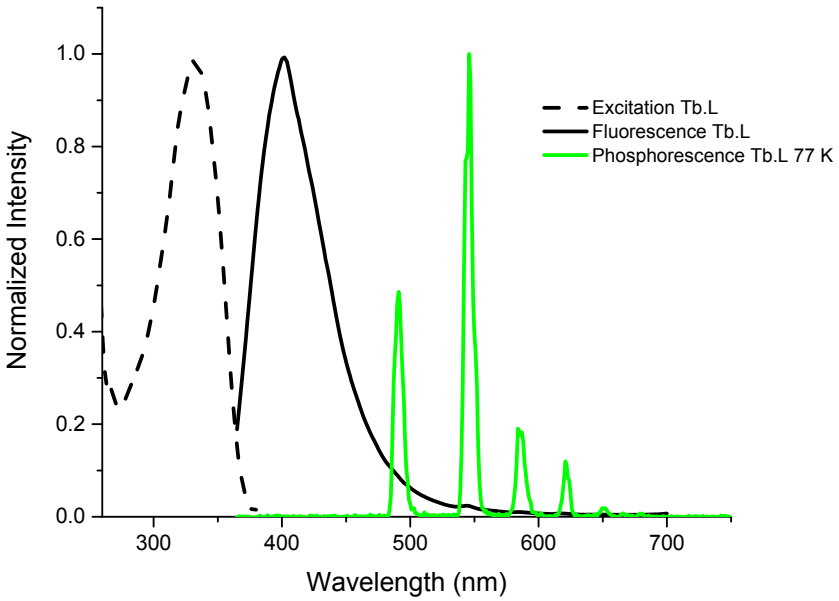


Figure S32. Excitation (followed at 402 nm) and emission (excitation 355 nm) spectra of a 1.14 $\cdot 10^{-5}$ M solution of **Tb.L** in HEPES buffer at pH 7.4 at room temperature. Phosphorescence spectrum of the same solution at 77 K, Gate time 1 ms, Delay 5 ms.

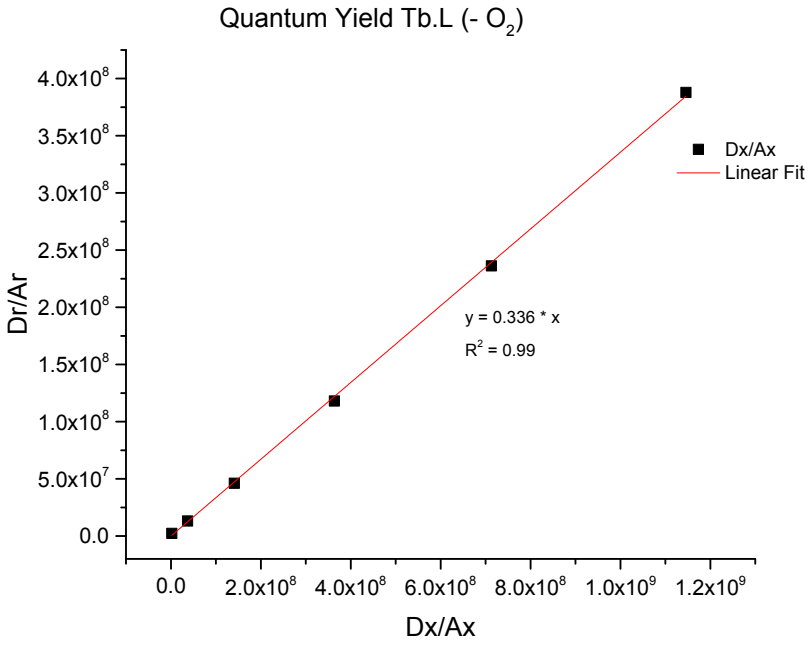


Figure S33. Quantum yield determination for **Tb.L** (- O_2) in 0.1 M HEPES buffer at pH 7.4 at room temperature.

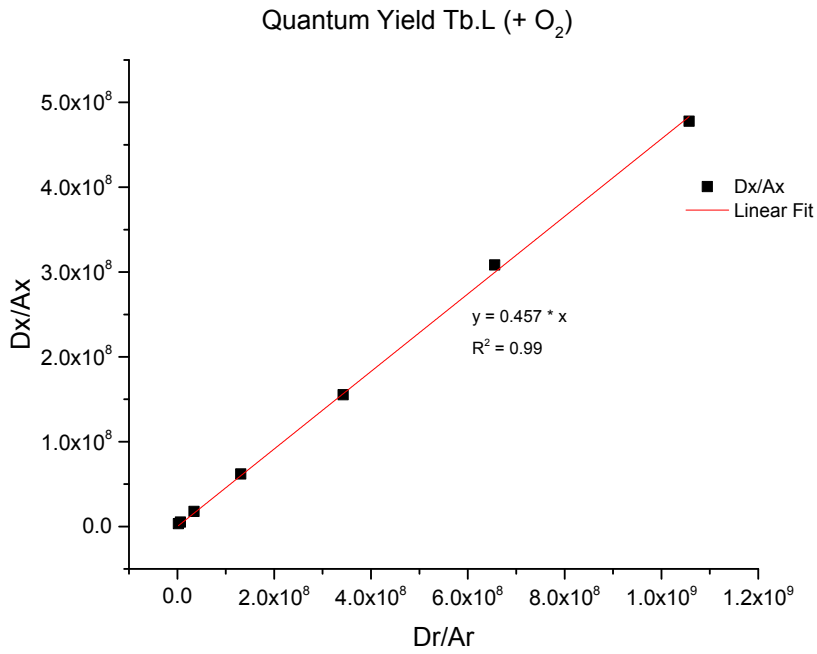
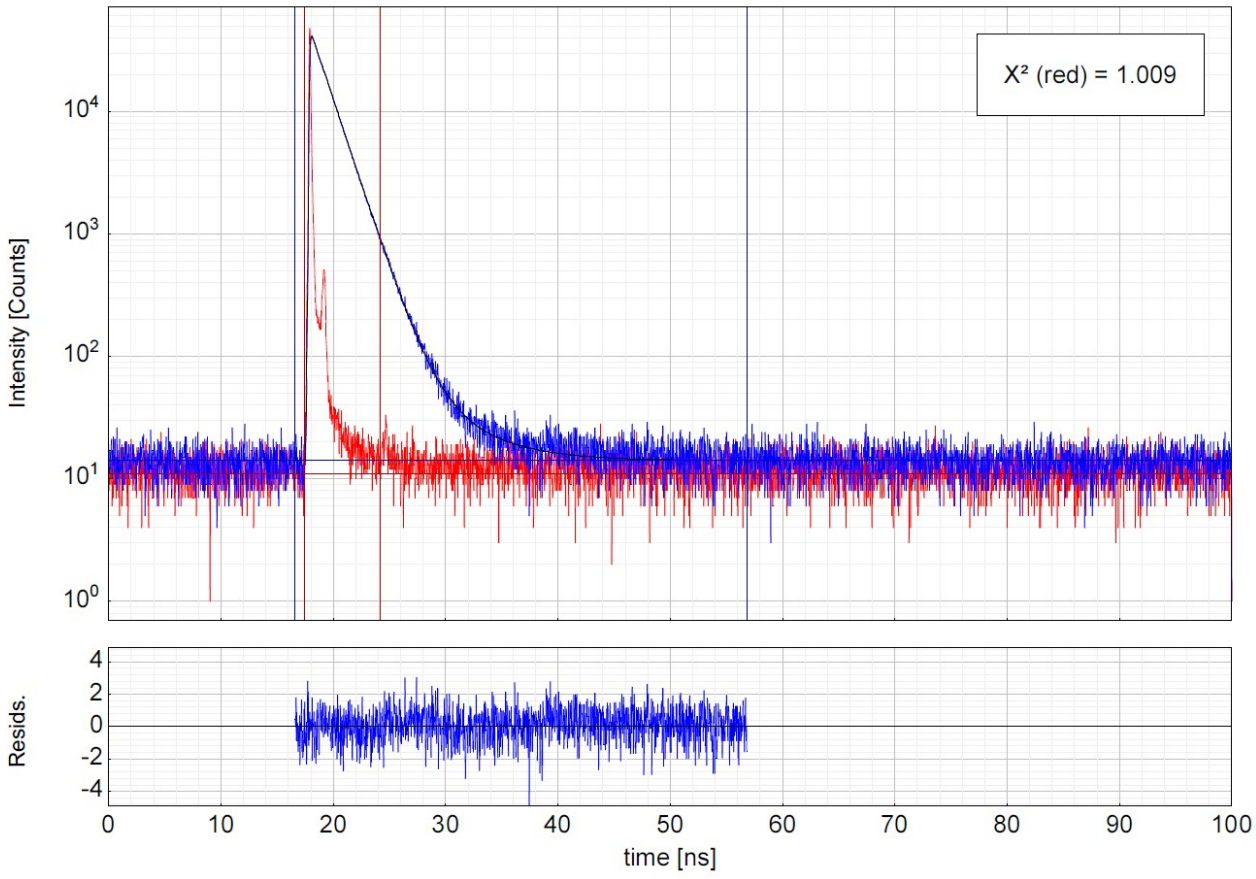


Figure S34. Quantum yield determination for **Tb.L** (+ O_2) in 0.1 M HEPES buffer at pH 7.4 at room temperature.



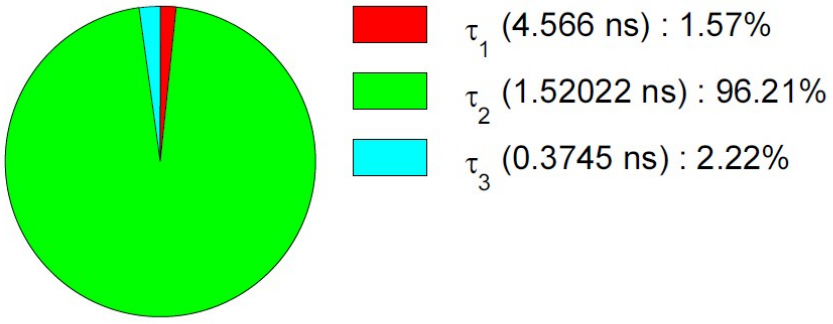
Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A_1 [Cnts]	297	-231	+231	Fitting
τ_1 [ns]	4.566	-0.128	+0.222	Support Plane
A_2 [Cnts]	54520	-1420	+1420	Fitting
τ_2 [ns]	1.52022	-0.00398	+0.00916	Support Plane
A_3 [Cnts]	5100	-4040	+4040	Fitting
τ_3 [ns]	0.3745	-0.0218	+0.0647	Support Plane
Bkgr. Dec [Cnts]	14.06	-5.56	+5.56	Fitting
Bkgr. IRF [Cnts]	11.1	-14.5	+14.5	Fitting
Shift IRF [ns]	-0.00764	-0.00839	+0.00839	Fitting
A Scat [Cnts]	-4790	-21900	+21900	Fitting

Average Lifetime:

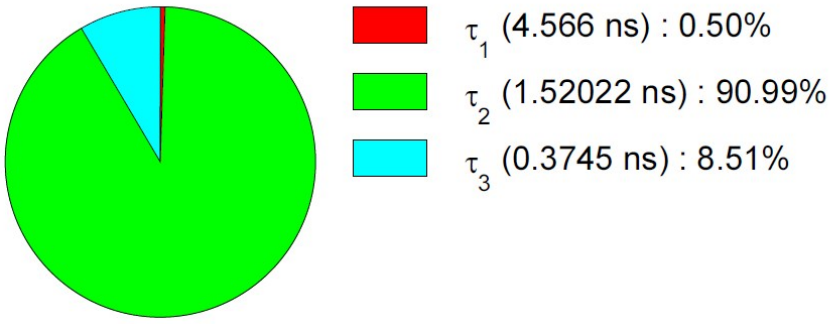
$\tau_{Av.1}$=1.543 ns (intensity weighted)

$\tau_{Av.2}$=1.438 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:



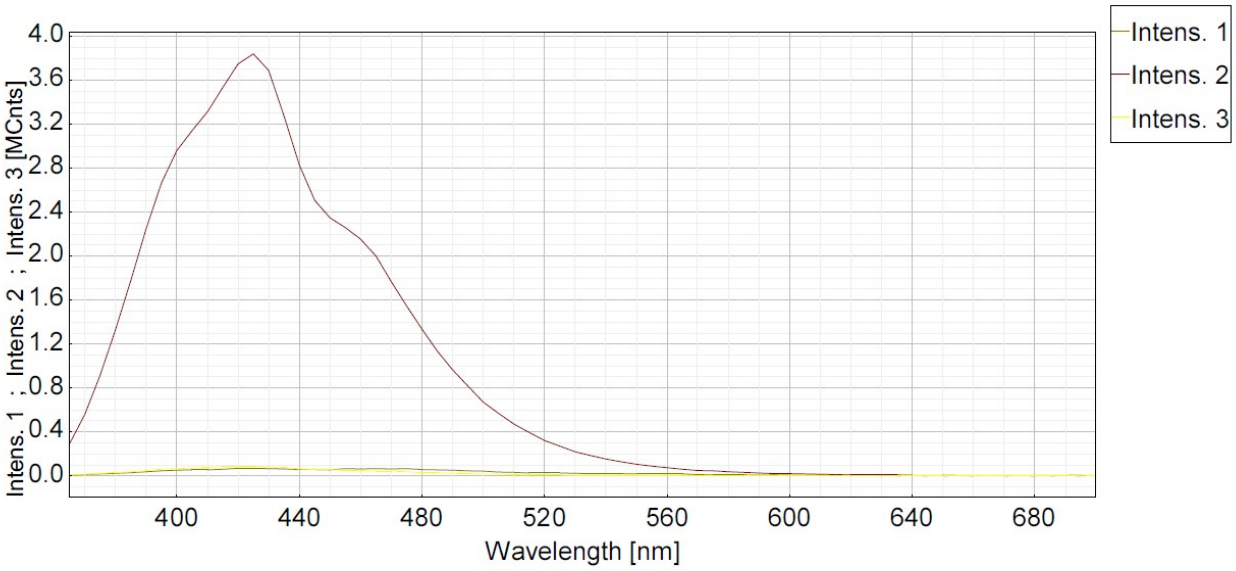
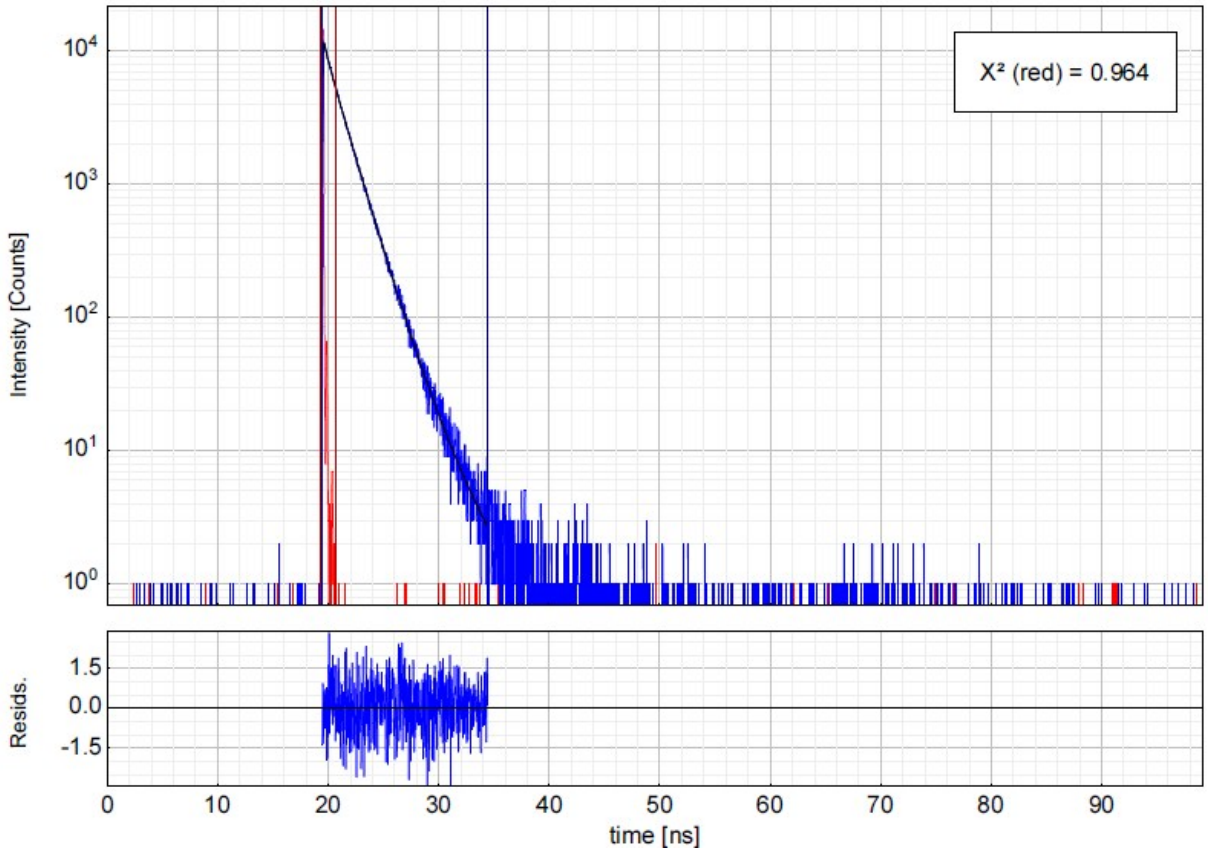


Figure S35. Fluorescence decay profile observed for **Tb.L** (-O_2) in HEPES Buffer pH 7.4. Top, time-resolved emission decay profile. Middle, result of global fit from time resolved emission spectra. Bottom, emission spectra deconvoluted using three lifetime components. The data was fitted to a triexponential decay to determine the associated lifetimes.



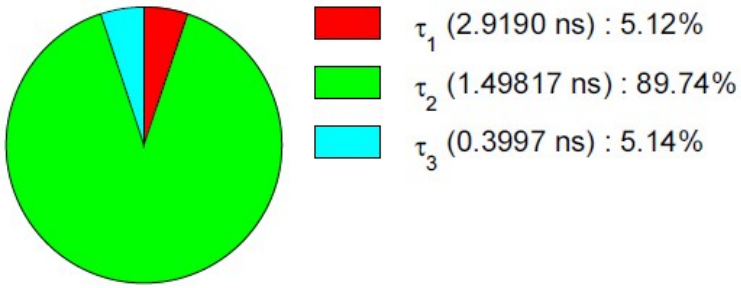
Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A_1 [Cnts]	302	-134	+134	Fitting
τ_1 [ns]	2.9190	-0.0861	+0.0706	Support Plane
A_2 [Cnts]	10310	-341	+341	Fitting
τ_2 [ns]	1.49817	-0.00900	+0.00651	Support Plane
A_3 [Cnts]	2214	-917	+917	Fitting
τ_3 [ns]	0.3997	-0.0355	+0.0281	Support Plane
Bkgr. Dec [Cnts]	0.280	-4.84	+4.84	Fitting
Bkgr. IRF [Cnts]	-25.8	-23.8	+23.8	Fitting
Shift IRF [ns]	2.36317	-0.00693	+0.00693	Fitting
A Scat [Cnts]	-1880	-3990	+3990	Fitting

Average Lifetime:

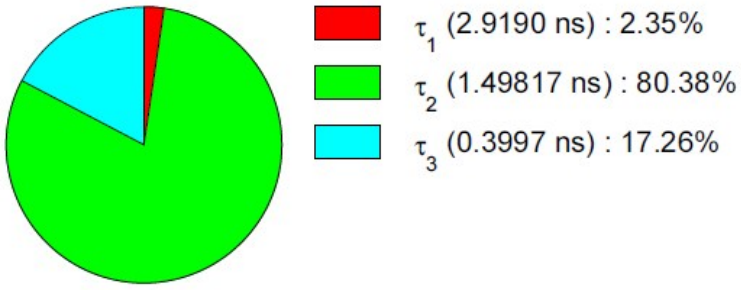
$\tau_{Av.1}$=1.5145 ns (intensity weighted)

$\tau_{Av.2}$=1.3420 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:



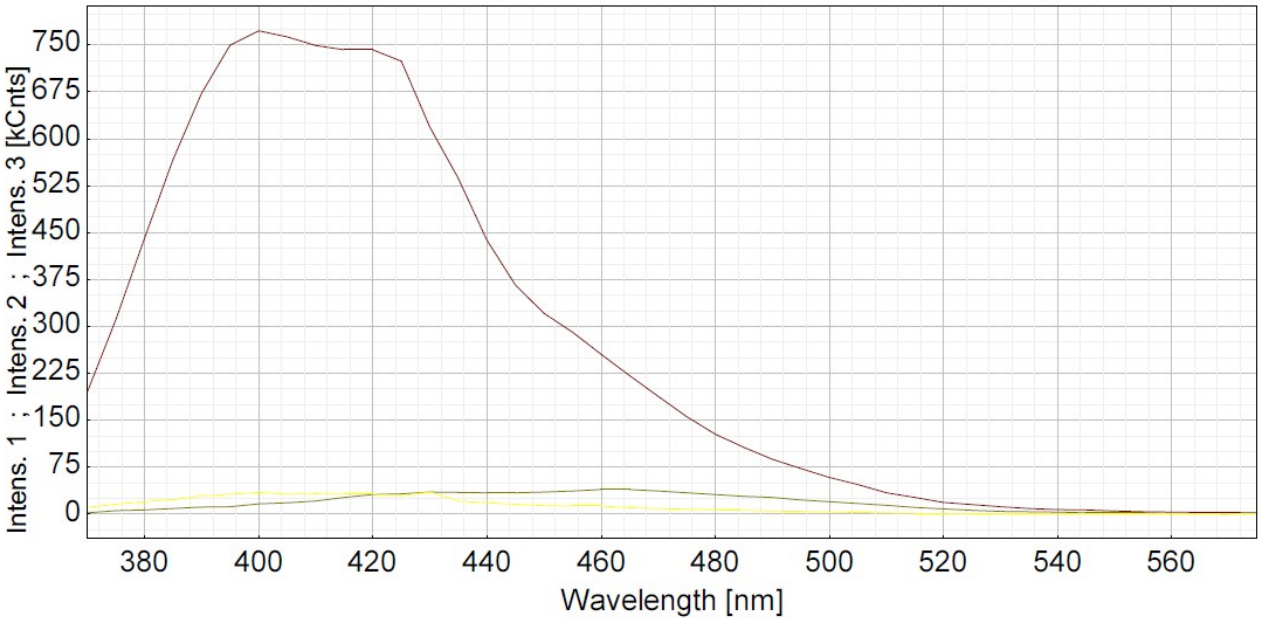


Figure S36. Fluorescence decay profile observed for **Tb.L** (-O_2) in HEPES Buffer pH 7.4. Top, time-resolved emission decay profile. Middle, result of global fit from time resolved emission spectra. Bottom, emission spectra deconvoluted using three lifetime components. The data was fitted to a triexponential decay to determine the associated lifetimes.

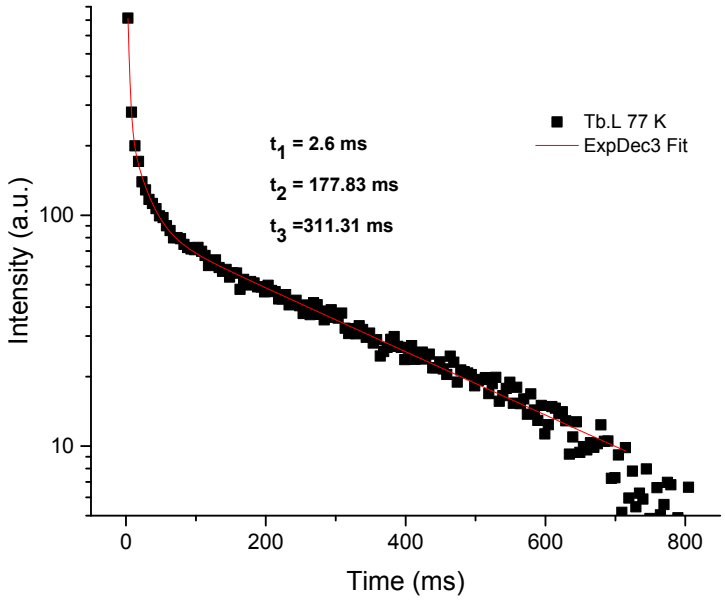


Figure S37. Time-resolved emission decay profile and fit for **Tb.L** at 77 K in HEPES buffer pH 7.4, monitored at 450 nm following 325 nm light excitation, Gate time 0.5 ms, Delay 5 ms, Total decay time 800 ms.

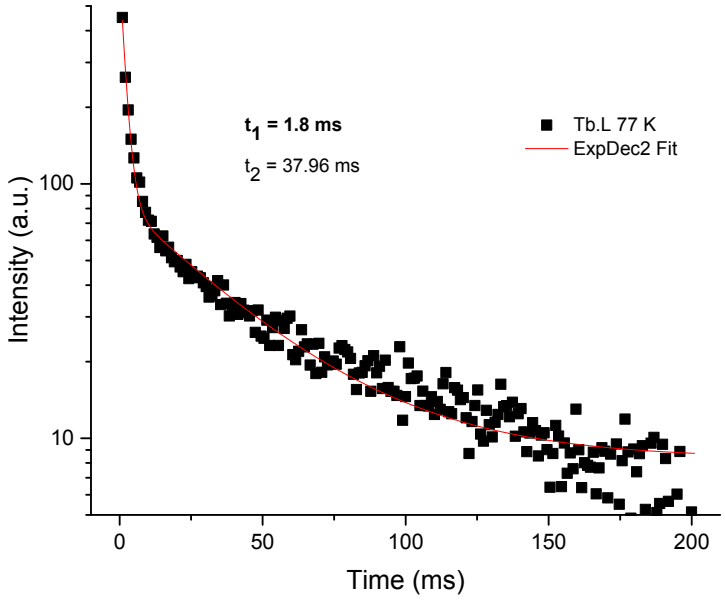


Figure S38. Time-resolved emission decay profile and fit for **Tb.L** at 77 K in HEPES buffer pH 7.4, monitored at 450 nm following 325 nm light excitation, Gate time 0.5 ms, Delay 1 ms, Total decay time 200 ms.

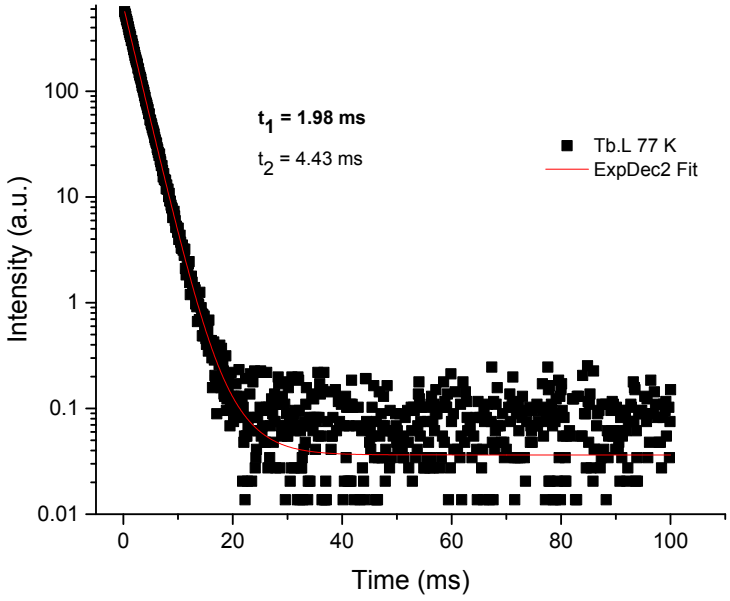


Figure S39. Time-resolved emission decay profile and fit for **Tb.L** at 77 K in HEPES buffer pH 7.4, monitored at 545 nm following 325 nm light excitation, Gate time 0.5 ms, Delay 0.1 ms, Total decay time 100 ms.

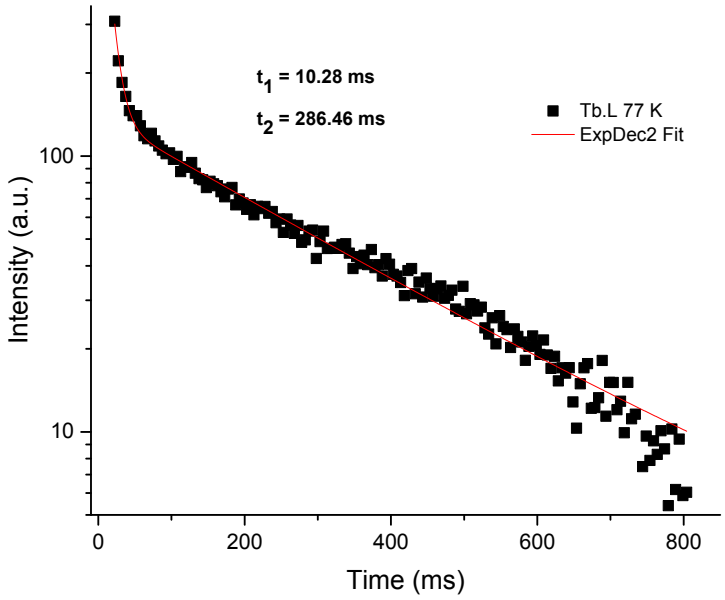


Figure S40. Time-resolved emission decay profile and fit for **Tb.L** at 77 K in HEPES buffer pH 7.4, monitored at 545 nm following 325 nm light excitation, Gate time 20 ms, Delay 5 ms, Total decay time 800 ms.

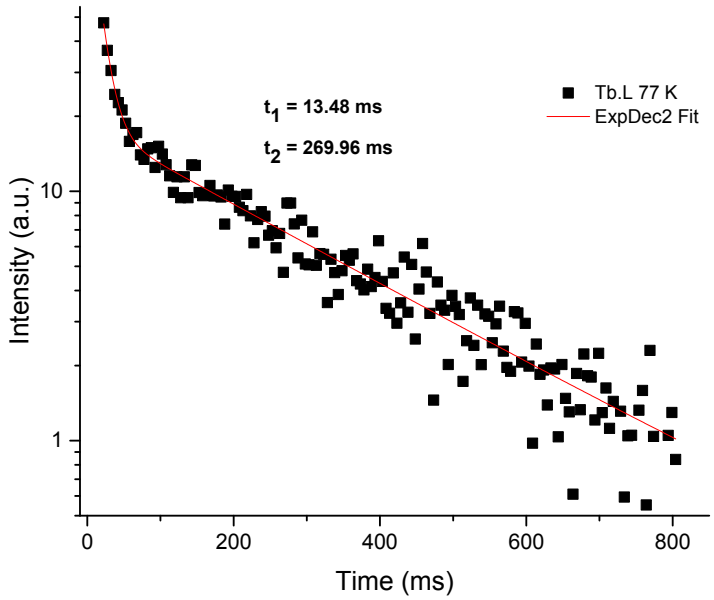


Figure S41. Time-resolved emission decay profile and fit for **Tb.L** at 77 K in HEPES buffer pH 7.4, monitored at 620 nm following 325 nm light excitation, Gate time 20 ms, Delay 5 ms, Total decay time 800 ms.

Optical Spectroscopy: Y.L

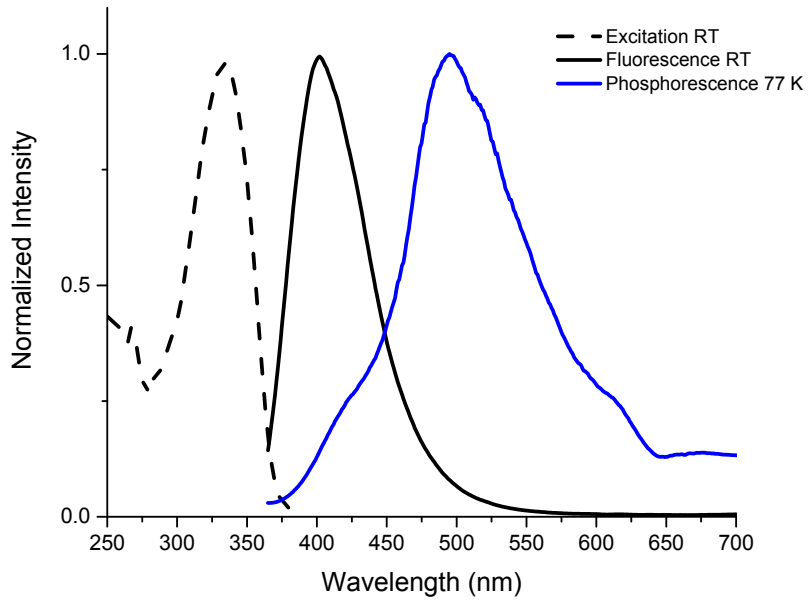


Figure S42. Excitation (followed at 402 nm) and emission (excitation 355 nm) spectra of a 1.14 $\cdot 10^{-5}$ M solution of **Y.L** in HEPES buffer at pH 7.4 at room temperature. Phosphorescence spectrum of the same solution at 77 K, Gate time 1 ms, Delay 5 ms.

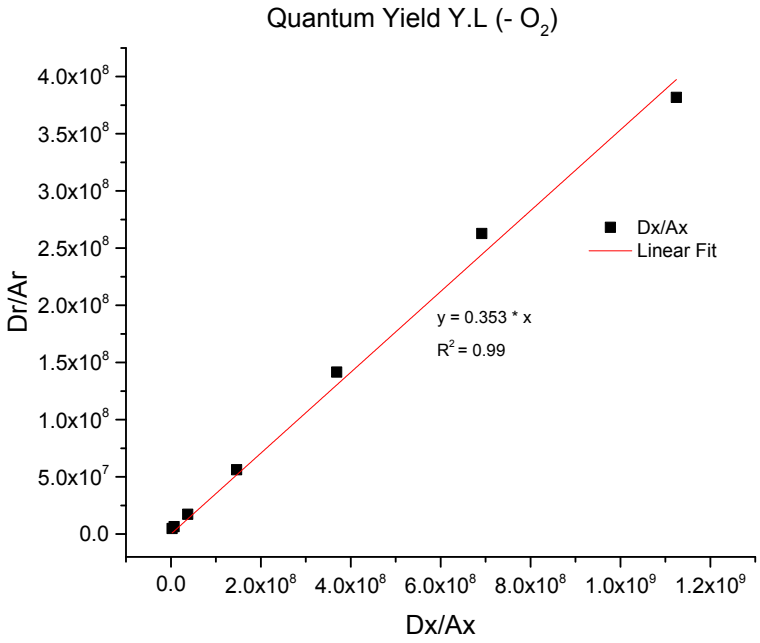


Figure S43. Quantum yield determination for **Y.L** (- O_2) in 0.1 M HEPES buffer at pH 7.4 at room temperature.

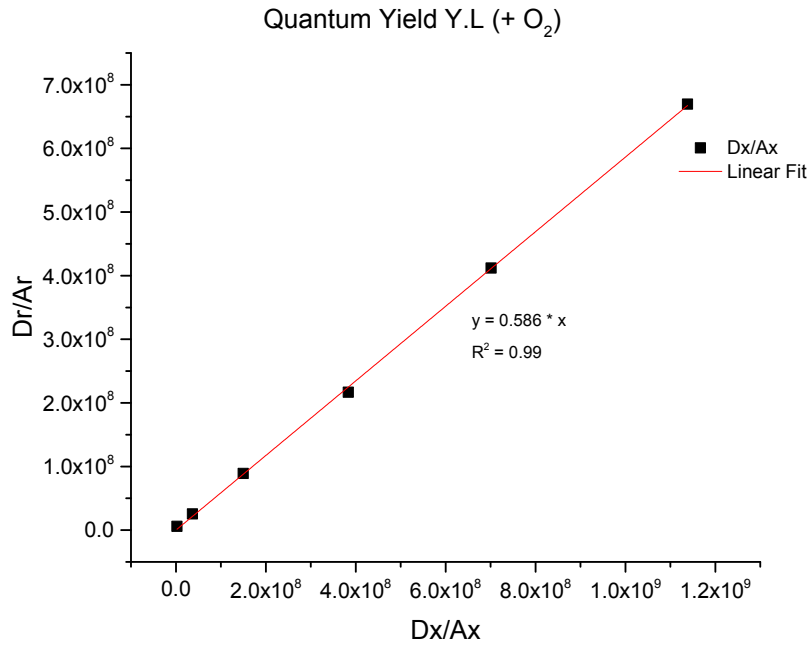
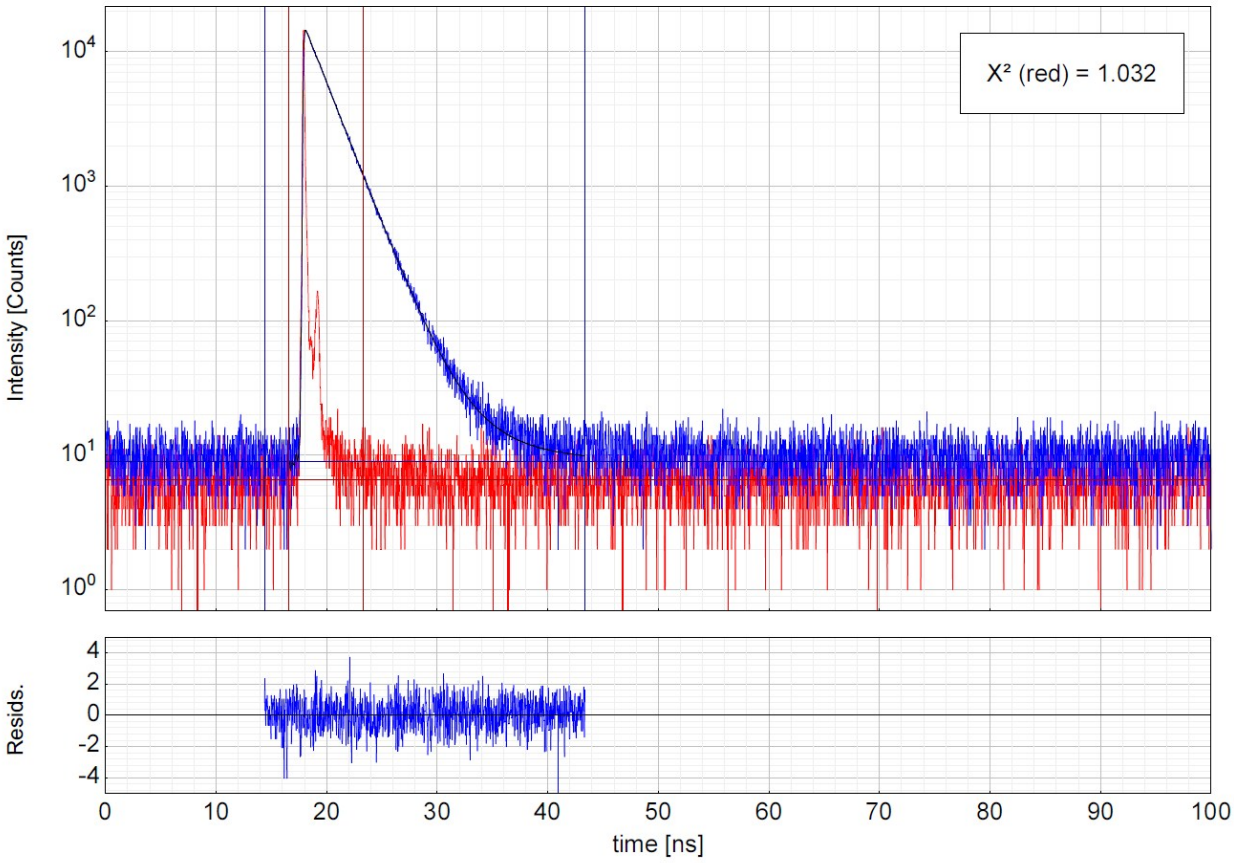


Figure S44. Quantum yield determination for **Y.L** (+ O_2) in 0.1 M HEPES buffer at pH 7.4 at room temperature.



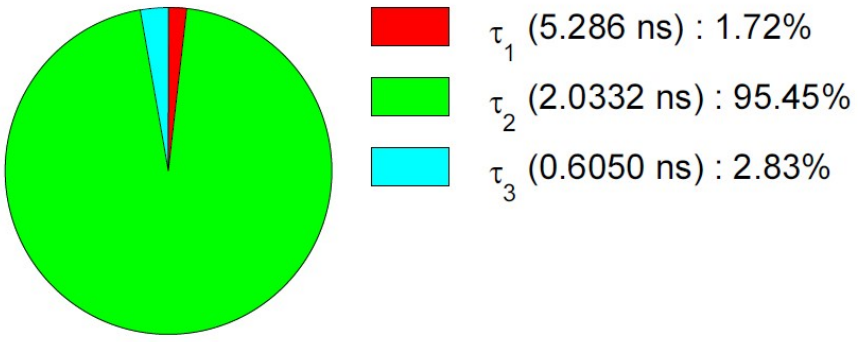
Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A_1 [Cnts]	138	-226	+226	Fitting
τ_1 [ns]	5.286	-0.215	+0.564	Support Plane
A_2 [Cnts]	19872	-981	+981	Fitting
τ_2 [ns]	2.0332	-0.0067	+0.0163	Support Plane
A_3 [Cnts]	1980	-2450	+2450	Fitting
τ_3 [ns]	0.6050	-0.0282	+0.0692	Support Plane
Bkgr. Dec [Cnts]	8.96	-8.21	+8.21	Fitting
Bkgr. IRF [Cnts]	6.63	-7.37	+7.37	Fitting
Shift IRF [ns]	-0.00469	-0.0151	+0.0151	Fitting
A Scat [Cnts]	-211	-17900	+17900	Fitting

Average Lifetime:

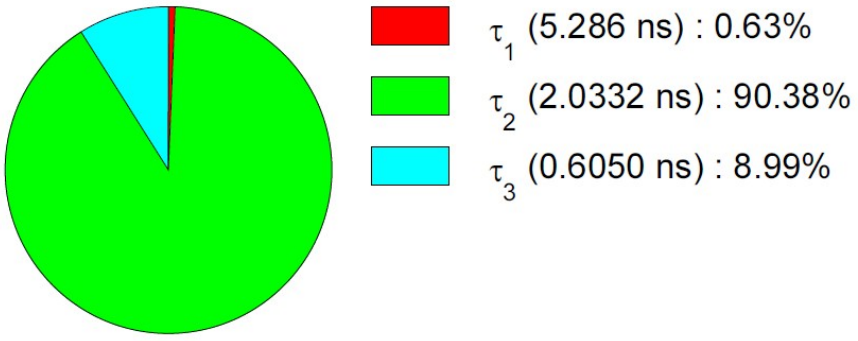
$\tau_{Av.1}$=2.049 ns (intensity weighted)

$\tau_{Av.2}$=1.925 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:



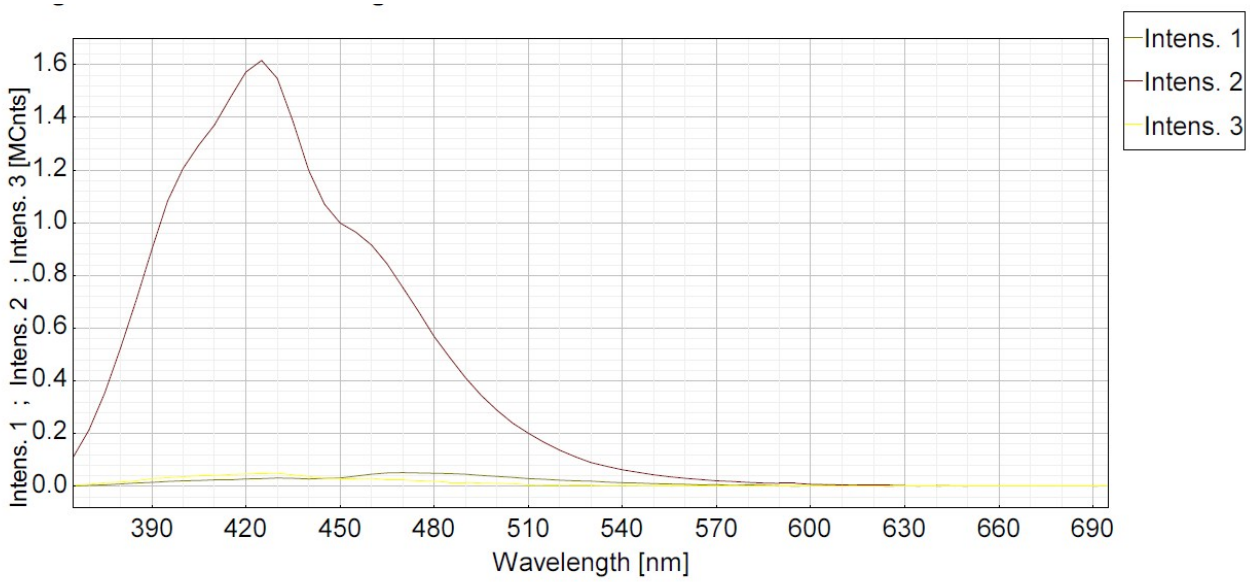
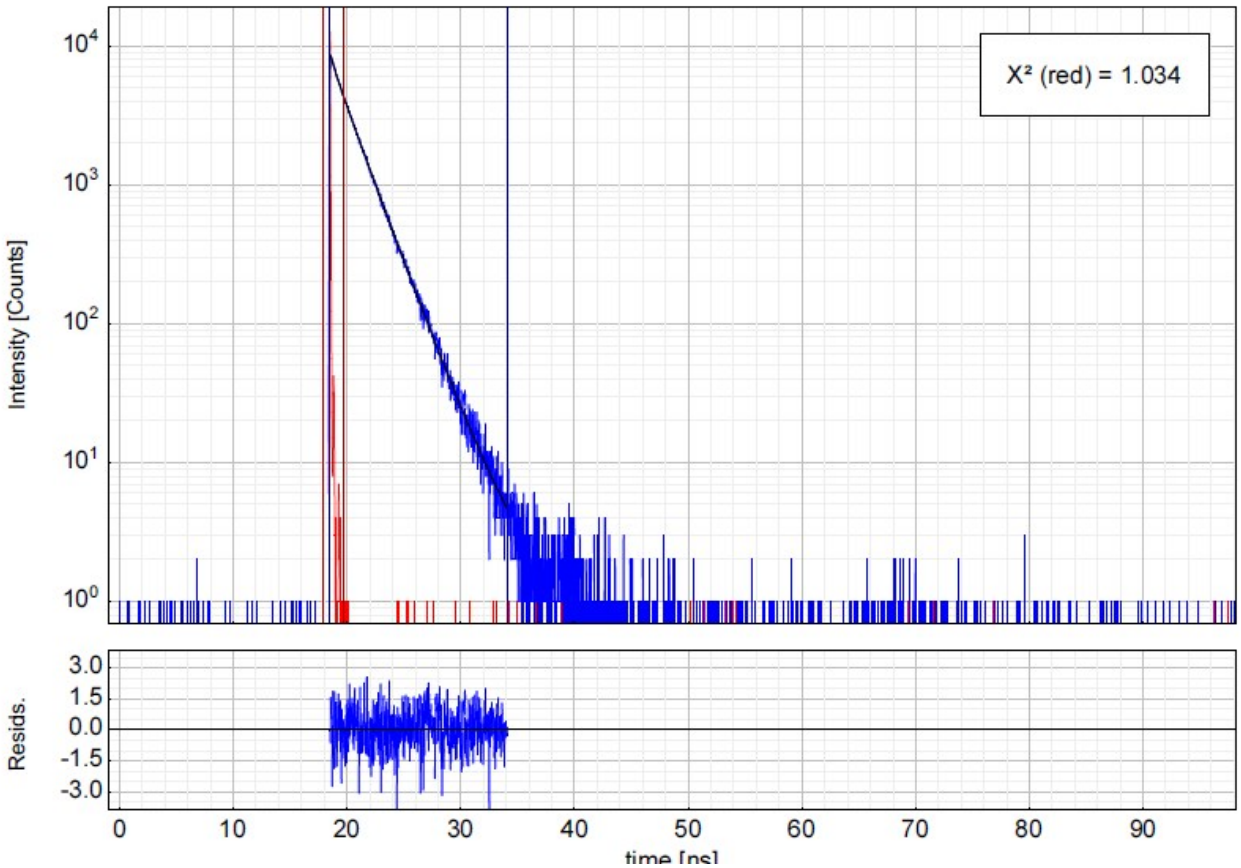


Figure S45. Fluorescence decay profile observed for **Y.L** (-O_2) in HEPES Buffer pH 7.4. Top, time-resolved emission decay profile. Middle, result of global fit from time resolved emission spectra. Bottom, emission spectra deconvoluted using three lifetime components. The data was fitted to a triexponential decay to determine the associated lifetimes.



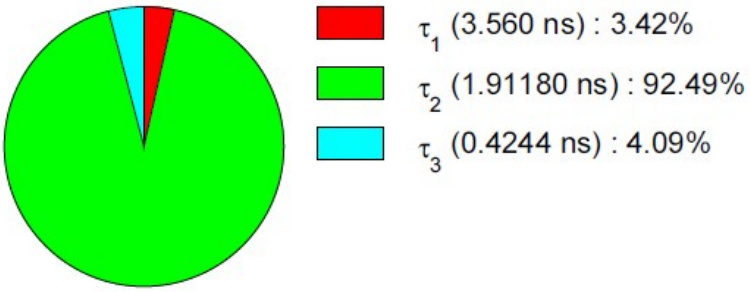
Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A_1 [Cnts]	151	-115	+115	Fitting
τ_1 [ns]	3.560	-0.157	+0.155	Support Plane
A_2 [Cnts]	7600	-271	+271	Fitting
τ_2 [ns]	1.91180	-0.00977	+0.00831	Support Plane
A_3 [Cnts]	1513	-828	+828	Fitting
τ_3 [ns]	0.4244	-0.0275	+0.0239	Support Plane
Bkgr. Dec [Cnts]	0.494	-6.30	+6.30	Fitting
Bkgr. IRF [Cnts]	-13.6	-18.8	+18.8	Fitting
Shift IRF [ns]	-0.9797	-0.0205	+0.0205	Fitting
A Scat [Cnts]	-433	-5310	+5310	Fitting

Average Lifetime:

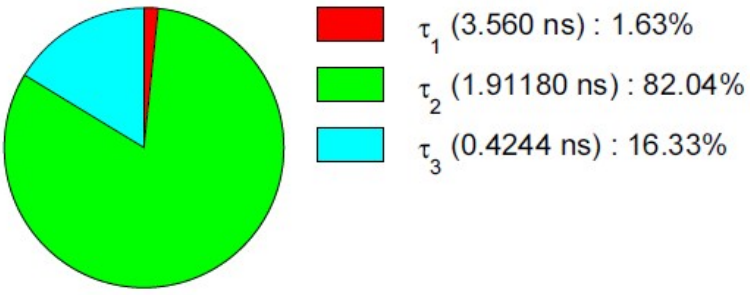
$\tau_{Av.1}$=1.907 ns (intensity weighted)

$\tau_{Av.2}$=1.696 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:



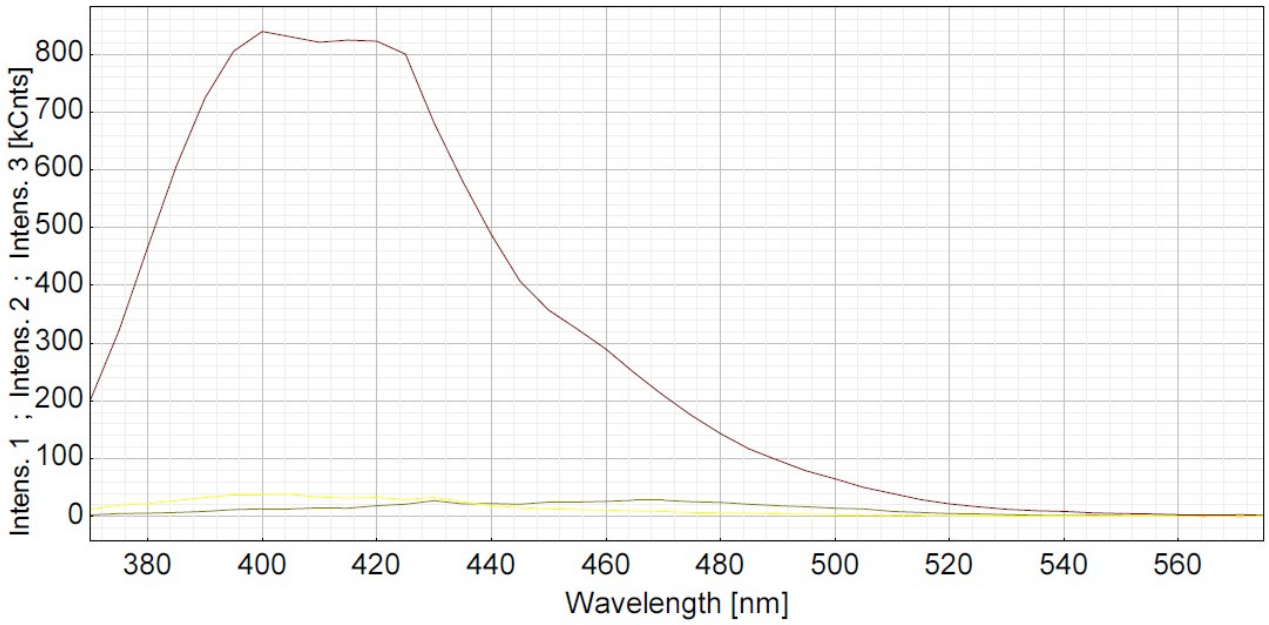


Figure S46. Fluorescence decay profile observed for **Y.L** (-O_2) in HEPES Buffer pH 7.4. Top, time-resolved emission decay profile. Middle, result of global fit from time resolved emission spectra. Bottom, emission spectra deconvoluted using three lifetime components. The data was fitted to a triexponential decay to determine the associated lifetimes.

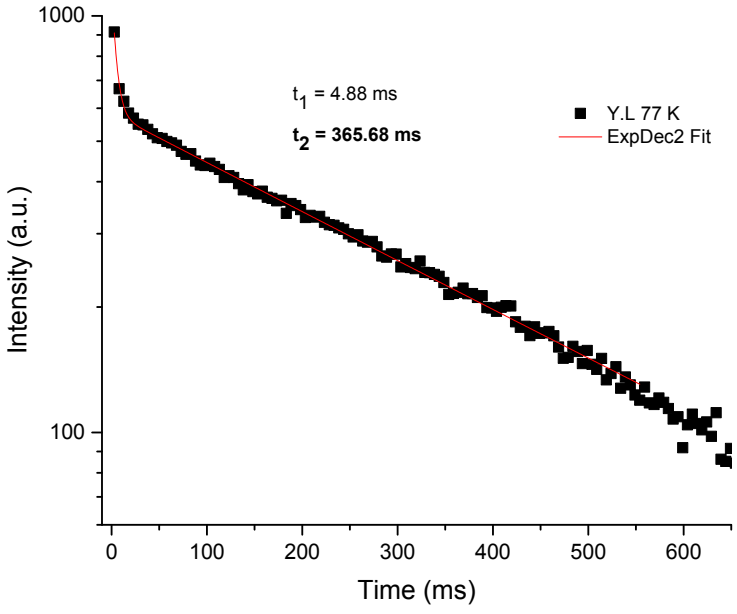


Figure S47. Time-resolved emission decay profile and fit for **Y.L** at 77 K in HEPES buffer pH 7.4, monitored at 500 nm following 325 nm light excitation, Gate time 0.1 ms, Delay 5 ms, Total decay time 800 ms.

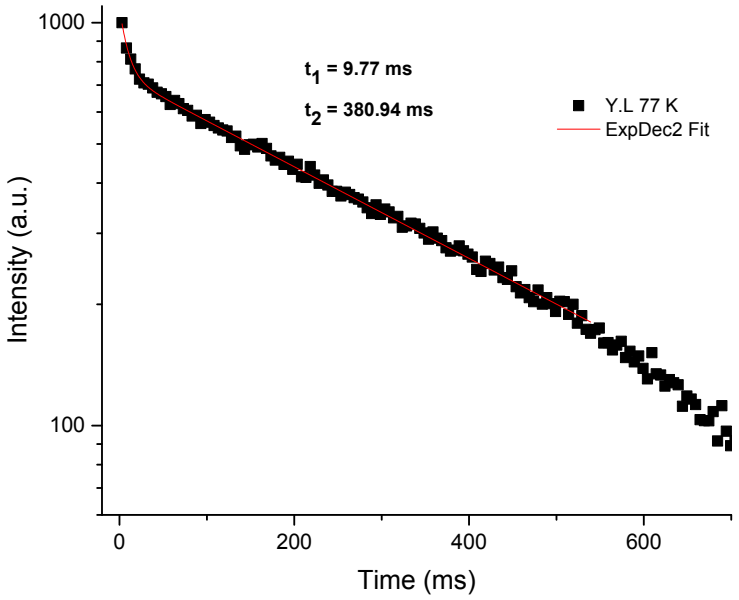


Figure S48. Time-resolved emission decay profile and fit for **Y.L** at 77 K in HEPES buffer pH 7.4, monitored at 500 nm following 325 nm light excitation, Gate time 0.5 ms, Delay 5 ms, Total decay time 800 ms.

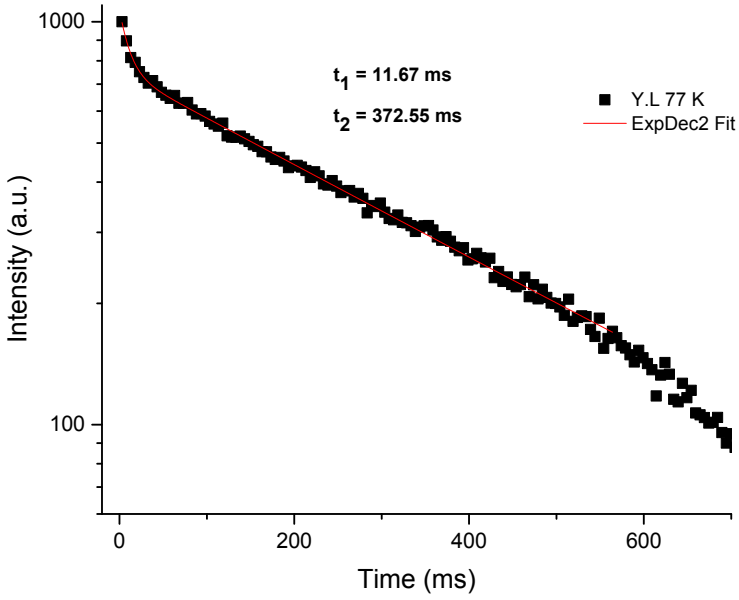


Figure S49. Time-resolved emission decay profile and fit for **Y.L** at 77 K in HEPES buffer pH 7.4, monitored at 500 nm following 325 nm light excitation, Gate time 0.5 ms, Delay 5 ms, Total decay time 800 ms.

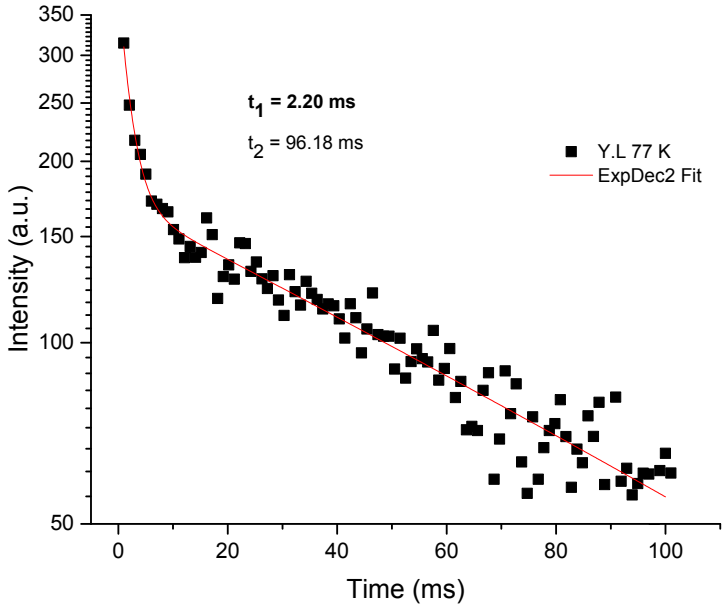


Figure S50. Time-resolved emission decay profile and fit for **Y.L** at 77 K in HEPES buffer pH 7.4, monitored at 500 nm following 325 nm light excitation, Gate time 0.1 ms, Delay 2 ms, Total decay time 100 ms.